# Lectures on Kinetic Theory of Gases and Statistical Physics

**(Oxford Physics Paper A1)**

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*(compiled on 20 February 2026)*

These are the notes for my lectures on Kinetic Theory and Statistical Physics, being part of the 2nd-year course (Paper A1) at Oxford. I taught the course in 2011-18, jointly with Professors Andrew Boothroyd (2011-15) and Julien Devriendt (2015-18), and since 2022 jointly with Professor Andrew Steane. Only my part of the course is covered in these notes. I will be grateful for any feedback from students, tutors or sympathisers.

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To play the good family doctor who warns about reading something prematurely, simply because it would be premature for him his whole life long—I'm not the man for that. And I find nothing more tactless and brutal than constantly trying to nail talented youth down to its "immaturity," with every other sentence a "that's nothing for you yet." Let him be the judge of that! Let him keep an eye out for how he manages.

Thomas Mann, *Doctor Faustus*

# PART I
# Basic Thermodynamics

*This part of the course was taught, in succession, by Professors Andrew Boothroyd, Julien Devriendt, and Andrew Steane.*

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Three Oxford versions of this material are available: the textbooks by Blundell & Blundell (2009) and Steane (2017), and the online lecture notes by Devriendt (2021) (which fill this and other gaps in my notes precisely). Besides and beyond these, for a very short and enlightened summary of basic thermodynamics, I recommend Chapter 1 of Kardar (2007). A good read, focused on entropy, is Ford (2013), Chapters 2 and 3. Another good read is the online lecture notes from the Other Place by Tong (2012), Chapter 4.

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# PART II
# Kinetic Theory

## 1. Statistical Description of a Gas

### 1.1. *Introduction*

You have so far encountered two basic types of physics:

1) Physics of single objects (or of groups of just a few such objects). For classical (*macroscopic*) objects, we had a completely deterministic description based on Newton's $2^{\text{nd}}$ Law: given initial positions and velocities of all participating objects and the forces acting on them (or between them), we could predict their behaviour forever. In the case of *microscopic* objects, this failed and had to be replaced by Quantum Mechanics—where, however, we again typically deal with single (or not very numerous) objects and can solve differential equations that determine, eventually, probabilities of quantum states (generalising the classical-mechanical notions of momentum, energy, angular momentum etc.)

2) Physics of "systems"—understood to be large collections of objects (e.g., gas is a large collection of particles). This was introduced in Part I—and the description of such systems seemed to be cast in completely different terms, the key notions being *internal energy*, *heat*, *temperature*, *entropy*, *volume*, *pressure*, etc. All these quantities were introduced largely without reference to the microscopic composition of the systems considered.

It is clear that a link between the two must exist—and we would like to understand how it works, both for our general peace of mind and for the purposes of practical calculation: for example, whereas the relationship between energy, heat, pressure and volume could be established and then the notions of temperature and entropy introduced without specifying what the system under consideration was made of, we had, in order to make practical quantitative predictions, to rely on experimentally determined empirical relations between

$$P, V, \text{ and } T \quad \text{(equation of state)}$$

and, $U$ being internal energy, between

$$U, V, \text{ and } T \quad \text{(often via the heat capacity, } C_V(T, V)\text{)}.$$

Statistical Mechanics (which we will study from Part III onwards) will deal with the question of how, given some basic microphysical information about properties of a system under consideration and some very general principles that a system *in equilibrium* must respect, we can derive the thermodynamics of the system (including, typically, $U(V, T)$, the equation of state $P(V, T)$, the entropy $S(V, T)$, and hence heat capacities, etc.).

Kinetic Theory (which we are about to study for the simple case of *classical monatomic ideal gas*) is concerned not just with the properties of systems in equilibrium but also—indeed, primarily—with *how the equilibrium is reached* and so how the collective properties of a system evolve with time. This will require both a workable (although not necessarily very detailed) model of the *constituent particles* of the system and of their *interaction (collisions)*. Equilibrium properties will also be derived, but with less generality than in Statistical Mechanics. We study Kinetic Theory first because it is somewhat less abstract and more intuitive than Statistical Mechanics (and we will recover all our *equilibrium* results later on in Statistical Mechanics). Also, it is convenient, in formulating Statistical Mechanics, to refer to some basic knowledge of Quantum Mechanics, whereas our Kinetic Theory will be completely classical.

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Whereas my exposition of Statistical Mechanics will be reasonably advanced, that of Kinetic Theory will be mostly quite elementary (except towards the end of §6). If you are looking for a more advanced treatment, I recommend the MMathPhys lecture notes by Dellar (2015) and/or (Chapter 1 of) the book by Lifshitz & Pitaevskii (1981).

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So how do we derive the behaviour of a macroscopic system from basic knowledge of the physics of its microscopic constituents?

Let us consider the simplest case: a classical gas. The simplest model is to assume that particles are hard spheres (billiard balls) and that their collisions are elastic (energy- and momentum-conserving). We will forget about Quantum Mechanics for now.

Suppose we know all of these particles' positions and velocities precisely at some time $t = 0$ (in fact, this is quite impossible even in principle, but we are ignoring Quantum Mechanics for now). Let us solve

$$m\ddot{\boldsymbol{r}} = \boldsymbol{F} \tag{1.1}$$

for each particle and thus obtain $\boldsymbol{r} = \boldsymbol{r}(t)$ and $\boldsymbol{v} = \dot{\boldsymbol{r}}(t)$ for all times $t > 0$. Problem solved? In fact, two difficulties arise:

1) There is too much information. A typical macroscopic gas system will have perhaps $10^{23}$ particles (**Exercise**: convince yourself that this is a reasonable estimate). Then one data dump ($\boldsymbol{r}$, $\boldsymbol{v}$ for each particle at one time $t$) needs about $\sim 10^{12}$ Tb. For comparison, all the world's data in 2025 amounted to $\sim 10^{11}$ Tb, so we need about 10 times that to save the state of air in a small box.

2) Sensitivity to initial conditions and tiny perturbations. This means that even if we could solve the equations of motions for all these particles, the tiniest errors or impre-

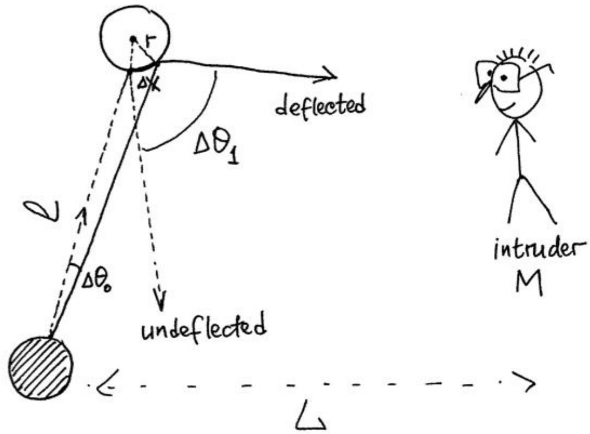


FIGURE 1. Billiard ball gravitationally deflected by an intruder.

cisions[1] would quickly change the solution, because any error in the initial conditions grows exponentially fast with time.

Let me give you an example to illustrate the last point.[2] Imagine we have a set of billiard balls on a frictionless table, we set them in motion (at $t = 0$) and want to observe them as time goes on. We could, in principle, solve their equations of motion and predict where they will all be and how fast they will be moving at any time $t > 0$. It turns out that if someone enters the room during this experiment, the small deflections of the balls due to the intruder's gravitational pull will accumulate to alter their trajectories completely after only $\sim 10$ collisions!

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**Proof** (Fig. 1). For simplicity of this very rough estimate, let us consider all the balls to be fixed in space, except for one, which moves and collides with them. Assume:

distance between balls $l \sim 20$ cm;
radius of a ball $r \sim 3$ cm;
size of the room $L \sim 5$ m;
mass of intruder $M \sim 80$ kg;
time between collisions $\Delta t \sim 1$ sec.

Then the deflection due to gravity after one collision is

$$\Delta x \sim \frac{MG}{L^2}\Delta t^2 \sim 10^{-8} \text{ cm}. \quad (1.2)$$

So the initial angular deflection is

$$\Delta\theta_0 \sim \frac{\Delta x}{l} \lll\lll\lll 1. \quad (1.3)$$

Angular deflection after the first collision:

$$\Delta\theta_1 \sim \frac{\Delta x}{r} \sim \Delta\theta_0 \, \frac{l}{r}. \quad (1.4)$$

We see that after each collision, the angular deflection will be amplified by a factor of $l/r$. Therefore, after $n$ collisions, it will be

$$\Delta\theta_n \sim \Delta\theta_0 \left(\frac{l}{r}\right)^n \sim \frac{\Delta x}{l}\left(\frac{l}{r}\right)^n. \quad (1.5)$$

[1] And of course any saved data will always have finite precision!

[2] I am grateful to G. Hammett for pointing out this example to me.

In order to estimate the number of collisions after which the trajectory changes significantly, we calculate $n$ such that $\Delta\theta_n \sim 1$:

$$n \sim \frac{\ln(l/\Delta x)}{\ln(l/r)} \sim 10, \quad \text{q.e.d.} \tag{1.6}$$

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The basic idea is that if errors grow exponentially with the number of collisions that a particle undergoes, you do not need very many collisions to amplify to order unity even very tiny initial perturbations (this is sometimes referred to as the "butterfly effect," after the butterfly that flaps its wings in India, producing a small perturbation that eventually precipitates a hurricane in Britain; cf. Bradbury 1952). A particle of air at 1 atm at room temperature has $\sim 10^9$ collisions per second (we will derive this in §4). Therefore, particle motion becomes essentially *random*—meaning chaotic, deterministically unpredictable in practice even for a classical system.

Thus, particle-by-particle deterministic description (1.1) is useless. Is this a setback? In fact, this is fine because we really are only interested in *bulk properties* of our system, not the motion of individual particles.[3] *If we can relate those bulk properties to averages over particle motion, we will determine everything we wish to know.*

Let us see how this is done.

### 1.2. *Energy*

So, we model our gas as a collection of moving point particles of mass $m$, *whose positions* $\boldsymbol{r}$ *and velocities* $\boldsymbol{v}$ *are random variables.* If we consider a volume of such a gas with no spatial inhomogeneities, then all positions $\boldsymbol{r}$ are equiprobable.

*The mean energy* of the $N$ particles comprising this system is

$$\langle E\rangle = N\left\langle\frac{mv^2}{2}\right\rangle, \tag{1.7}$$

where $\langle mv^2/2\rangle$ is the mean energy of a particle and we assume that all particles have the same statistical distribution of velocities. In general, particles may have a *mean velocity*, i.e., the whole system may be moving at some speed in some direction:

$$\langle\boldsymbol{v}\rangle = \boldsymbol{u}. \tag{1.8}$$

Let $\boldsymbol{v} = \boldsymbol{u} + \boldsymbol{w}$, where $\boldsymbol{w}$ is *peculiar velocity*, for which $\langle\boldsymbol{w}\rangle = 0$ by definition. Then

$$\langle E\rangle = N\frac{m}{2}\left\langle|\boldsymbol{u}+\boldsymbol{w}|^2\right\rangle = \underbrace{\frac{Mu^2}{2}}_{\equiv K} + \underbrace{N\left\langle\frac{mw^2}{2}\right\rangle}_{\equiv U}, \tag{1.9}$$

where $M = Nm$. The energy consists of the kinetic energy of the system as a whole, $K$, and the *internal energy*, $U$. It is $U$ that appears in thermodynamics ("heat")—the *mean energy of the disordered motion of the particles* ("invisible motion," as they called it in the 19$^{\rm th}$ century). The motion is disordered in the sense that it is random and has zero

[3]We will learn in §11.8 that, in fact, talking about the behaviour of individual particles in a gas is meaningless anyway, because particles are usually indistinguishable.

mean: $\langle \boldsymbol{w} \rangle = 0$. For now, we will assume $\boldsymbol{u} = 0$[4] and so

$$U = \langle E \rangle = N \left\langle \frac{mv^2}{2} \right\rangle. \tag{1.10}$$

## 1.3. *Thermodynamic Limit*

Is it really enough to know the *average* energy of the system? How is this average energy $U$ related to the system's *exact* energy $E$? If they could be very different at any given instance, then, clearly, knowing only $U$ would leave us fairly ignorant about the system's actual state. Here we are greatly helped by what we previously thought made the description of the system difficult—the very large $N$. It turns out that for $N \gg 1$, the typical difference between the average energy and the exact energy is very small (and the same will be true about all the other relevant bulk quantities that can be referred to some microscopically exact values).

Let us estimate this difference. The mean energy is $U = \langle E \rangle$ and the exact energy is

$$E = \sum_i \frac{mv_i^2}{2}, \tag{1.11}$$

where the index $i$ runs through all $N$ particles in the system and $\boldsymbol{v}_i$ is the velocity of the $i$th particle. Then the mean square energy fluctuation is

$$\begin{aligned}\left\langle (E-U)^2 \right\rangle = \langle E^2 \rangle - U^2 &= \sum_{i,j} \left\langle \frac{mv_i^2}{2} \frac{mv_j^2}{2} \right\rangle - \left( \sum_i \left\langle \frac{mv_i^2}{2} \right\rangle \right)^2 \\ &= \sum_i \left\langle \frac{m^2 v_i^4}{4} \right\rangle + \sum_{i \neq j} \left\langle \frac{mv_i^2}{2} \right\rangle \left\langle \frac{mv_j^2}{2} \right\rangle - \left( \sum_i \left\langle \frac{mv_i^2}{2} \right\rangle \right)^2 \\ &= N \left\langle \frac{m^2 v^4}{4} \right\rangle + N(N-1) \left\langle \frac{mv^2}{2} \right\rangle^2 - \left( N \left\langle \frac{mv^2}{2} \right\rangle \right)^2 \\ &= N \frac{m^2}{4} \left( \langle v^4 \rangle - \langle v^2 \rangle^2 \right). \end{aligned} \tag{1.12}$$

Note that, in the second line of this calculation, we are allowed to write $\langle v_i^2 v_j^2 \rangle = \langle v_i^2 \rangle \langle v_j^2 \rangle$ for $i \neq j$ only if we assume that *velocities of different particles are independent random variables*, an important caveat. From (1.12), we find that the relative root-mean-square fluctuation of energy is

$$\frac{\Delta E_{\rm rms}}{U} \equiv \frac{\left\langle (E-U)^2 \right\rangle^{1/2}}{U} = \frac{\left[ N(m^2/4) \left( \langle v^4 \rangle - \langle v^2 \rangle^2 \right) \right]^{1/2}}{N \langle mv^2/2 \rangle} = \left( \frac{\langle v^4 \rangle}{\langle v^2 \rangle^2} - 1 \right)^{1/2} \frac{1}{\sqrt{N}} \ll 1. \tag{1.13}$$

This is very small for $N \gg 1$ because the prefactor in the above formula is clearly independent of $N$, as it depends only on single-particle properties, viz., the moments $\langle v^2 \rangle$ and $\langle v^4 \rangle$ of a particle's velocity.

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**Exercise 1.1.** If you like mathematical exercises, figure out how to prove that $\langle v^4 \rangle \geqslant \langle v^2 \rangle^2$, whatever is the distribution of $v$—so we are not taking the square root of a negative number! What is the exact prefactor of $1/\sqrt{N}$ in (1.13) for a Gaussian distribution of $\boldsymbol{v}$ in 3D? [See (2.15).]

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[4] Since we have already assumed that the system is homogeneous, we must have $\boldsymbol{u} = \text{const}$ across the system and so, if $\boldsymbol{u}$ is also constant in time, we can just go to a frame moving with velocity $\boldsymbol{u}$. I will relax the homogeneity assumption in §5.

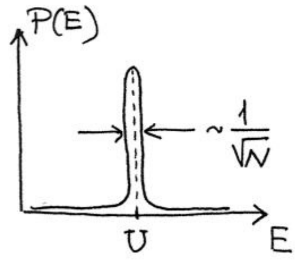


FIGURE 2. Thermodynamic limit, $N \gg 1$: the probability distribution $P(E)$ of the exact quantity (here energy $E$) is sharply peaked around its mean.

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The result (1.13) implies that the distribution of the system's total energy $E$ (which is a random variable[5] because particle velocities are random variables) is very sharply peaked around its mean $U = \langle E\rangle$: the width of this peak is $\sim \Delta E_{\rm rms}/U \sim 1/\sqrt{N} \ll 1$ for $N \gg 1$ (Fig. 2). This is called the *thermodynamic limit*—the statement that mean quantities for systems of very many particles approximate extremely well the exact properties of the system.[6]

I hope to have convinced you that *averages* do give us a good representation of the actual state of the system, at least when the number of constituent particles is large.

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**Exercise 1.2.** Consider a large system of volume $\mathcal{V}$ containing $\mathcal{N}$ non-interacting particles. Take some fixed subvolume $V \ll \mathcal{V}$. Calculate the probability to find $N$ particles in the subvolume $V$. Then assume that both $\mathcal{N}$ and $\mathcal{V}$ tend to $\infty$, but in such a way that the particle number density is fixed: $\mathcal{N}/\mathcal{V} \to n = \text{const}$.

(a) Show that in this limit, the probability $p_N$ to find $N$ particles in volume $V$ (both $N$ and $V$ are fixed, $N \ll \mathcal{N}$) tends to the Poisson distribution whose average is $\langle N\rangle = nV$. *Hint.* This involves proving Poisson's limit theorem. You will find inspiration or possibly even the solution in standard probability texts (a particularly good one is Sinai 1992).

(b) Prove that

$$\frac{\left\langle (N - \langle N\rangle)^2\right\rangle^{1/2}}{\langle N\rangle} = \frac{1}{\sqrt{\langle N\rangle}} \tag{1.14}$$

(so fluctuations around the average are very small if $\langle N\rangle \gg 1$).

(c) Show that, if $\langle N\rangle \gg 1$, $p_N$ has its maximum at $N \approx \langle N\rangle = nV$; then show that in the vicinity of this maximum, the distribution of $N$ is Gaussian:

$$p_N \approx \frac{1}{\sqrt{2\pi nV}}\, e^{-(N-nV)^2/2nV}. \tag{1.15}$$

*Hint.* Use Stirling's formula for $N!$, Taylor-expand $\ln p_N$ around $N = nV$.

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[5]Unless the system is completely isolated, in which case $E = \text{const}$ (see §12.1.2). However, completely isolated systems do not really exist (or are, at any rate, inaccessible to observation, on account of being completely isolated) and it tends to be more interesting and more useful to think of systems in which some exchange with the outside world is permitted and only mean quantities, in particular the mean energy, are fixed, in the sense of being accesible to measurement (§9).

[6]This may break down if there are strong correlations between particles, i.e., $\langle v_i^2 v_j^2\rangle \neq \langle v_i^2\rangle\langle v_j^2\rangle$: indeed, as I noted after (1.12), our result is only valid if the averages can be split. Fluctuations in *strongly coupled systems*, where the averages cannot be split, can be very strong. This is why we focus on the "ideal gas" (non-interacting particles; see §2).

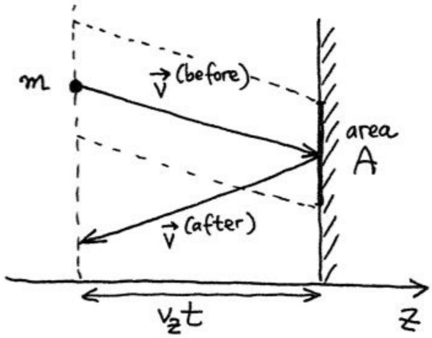


FIGURE 3. Kinetic calculation of pressure. Particles within the volume $Av_z t$ will hit area $A$ during time $t$ and bounce, each delivering momentum $2mv_z$ to the wall.

The result of (a) is, of course, intuitively obvious, but it is nice to be able to prove it mathematically and even to work out with what precision it holds, as you have done in (b)—another demonstration that the world is constructed in a sensible way.

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## 1.4. *Kinetic Calculation of Pressure*

[Literature: Pauli (2003), §24]

Our objective now is to work out how an important bulk property of a volume of gas—pressure $P$ felt by the walls of a container (or by a body immersed in the gas, or by an imaginary surface separating one part of the gas from another)—is related to average properties of the velocity distribution of the moving particles.

Particles hit a surface (wall) and bounce off; we assume that they do it *elastically.* Recall that

pressure = force per unit area,

force = momentum per unit time.

Therefore, pressure on the wall is the momentum delivered to the wall by the bouncing particles per unit time per unit area ("*momentum flux*").[7]

Let $z$ be the direction perpendicular to the wall (Fig. 3). When a particle bounces off the wall, the projection of its velocity on the $z$ axis changes sign,

$$v_z^{(\text{after})} = -v_z^{(\text{before})}, \tag{1.16}$$

while the two other components of the velocity ($v_x$ and $v_y$) are unchanged. Therefore, the momentum delivered by the particle to the wall is

$$\Delta p = 2mv_z. \tag{1.17}$$

Consider the particles the $z$ component of whose velocity lies in a small interval $[v_z, v_z + \mathrm{d}v_z]$, where $\mathrm{d}v_z \ll v_z$. Then the contribution of these particles to pressure is

$$\mathrm{d}P(v_z) = \Delta p\, \mathrm{d}\Phi(v_z) = 2mv_z \mathrm{d}\Phi(v_z), \tag{1.18}$$

where $\mathrm{d}\Phi(v_z)$ is the differential *particle flux*, i.e., the number of particles with velocities

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[7]Technically, each particle, as it bounces, exerts on the wall an infinite force for zero time, but we will add, and average over, many of these instantaneous kicks and get a finite answer.

in the interval $[v_z, v_z + \mathrm{d}v_z]$ hitting the wall per unit time per unit area. In other words, if we consider a wall area $A$ and time $t$, then

$$\mathrm{d}\Phi(v_z) = \frac{\mathrm{d}N(v_z)}{At}. \tag{1.19}$$

Here $\mathrm{d}N(v_z)$ is the number of particles with velocity in the interval $[v_z, v_z + \mathrm{d}v_z]$ that hit area $A$ over time $t$:

$$\mathrm{d}N(v_z) = Av_z t \cdot n \cdot f(v_z)\mathrm{d}v_z, \tag{1.20}$$

where $Av_z t$ is the volume where a particle with velocity $v_z$ must be to hit the wall during time $t$, $n = N/V$ is the number density of particles in the gas and $f(v_z)\mathrm{d}v_z$ is, by definition, the fraction of particles whose velocities are in the interval $[v_z, v_z + \mathrm{d}v_z]$. The differential particle flux is, therefore,

$$\mathrm{d}\Phi(v_z) = nv_z f(v_z)\mathrm{d}v_z \tag{1.21}$$

(perhaps this is just obvious without the lengthy explanation).

We have found that we need to know the *particle distribution function* ("pdf") $f(v_z)$, which is the *probability density function* (also "pdf") of the velocity distribution for a single particle—i.e., the fraction of particles in our infinitesimal interval, $f(v_z)\mathrm{d}v_z$, is the *probability* for a single particle to have its velocity in this interval.[8] As always in probability theory, the normalisation of the pdf is

$$\int_{-\infty}^{+\infty} f(v_z)\mathrm{d}v_z = 1 \tag{1.22}$$

(the probability for a particle to have some velocity between $-\infty$ and $+\infty$ is 1). We assume that all particles have the same velocity pdf: there is nothing special, statistically, about any given particle or subset of particles and they are all in equilibrium with each other.

From (1.18) and (1.21), we have

$$\mathrm{d}P(v_z) = 2mnv_z^2 f(v_z)\mathrm{d}v_z. \tag{1.23}$$

To get the total pressure, we integrate this over all particles with $v_z > 0$ (those that are moving towards the wall rather than away from it):

$$P = \int_0^{\infty} 2mnv_z^2 f(v_z)\mathrm{d}v_z. \tag{1.24}$$

Let us further assume that $f(v_z) = f(-v_z)$, i.e., that there is no preference for motion in any particular direction (e.g., the wall is not attractive). Then

$$P = mn\int_{-\infty}^{+\infty} v_z^2 f(v_z)\mathrm{d}v_z = mn\langle v_z^2\rangle. \tag{1.25}$$

The pdf that I have introduced was in 1D, describing particle velocities in one direction only. It is easily generalised to 3D: let me introduce $f(v_x, v_y, v_z)$, which I will abbreviate as $f(\boldsymbol{v})$, such that $f(\boldsymbol{v})\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ is the probability for the particle velocity to be in the "cube" $\boldsymbol{v} \in [v_x, v_x + \mathrm{d}v_x] \times [v_y, v_y + \mathrm{d}v_y] \times [v_z, v_z + \mathrm{d}v_z]$ (mathematically speaking, this a *joint probability* for three random variables $v_x$, $v_y$ and $v_z$). Then the 1D pdf of $v_z$ is

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[8] In §12.2, we will examine somewhat more critically this "frequentist" interpretation of probabilities. A more precise statistical-mechanical definition of $f(v_z)$ will be given in §11.11.

simply

$$f(v_z) = \int_{-\infty}^{+\infty} \mathrm{d}v_x \int_{-\infty}^{+\infty} \mathrm{d}v_y f(v_x, v_y, v_z). \tag{1.26}$$

Therefore, the pressure is

$$\boxed{P = mn \int \mathrm{d}^3\boldsymbol{v}\, v_z^2 f(\boldsymbol{v}) = mn\langle v_z^2\rangle}\,. \tag{1.27}$$

So the pressure on a wall is simply proportional to the mean square $z$ component of the velocity of the particles, where $z$, by definition, is the direction perpendicular to the wall on which we are calculating the pressure.[9]

## 1.5. *Isotropic Distributions*

Let us now make a further assumption: all directions are statistically the same, the system is *isotropic* (there are no special directions). Then

$$\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \frac{1}{3}\langle v^2\rangle \tag{1.28}$$

because $v^2 = v_x^2 + v_y^2 + v_z^2$. Therefore, from (1.27),

$$\boxed{P = \frac{1}{3}\,mn\langle v^2\rangle = \frac{2}{3}\frac{U}{V}}\,, \tag{1.29}$$

where $V$ is the volume of the system and $U$ is its mean internal energy (defined in §1.3). We have discovered the interesting result that in isotropic, 3D systems, pressure is equal to 2/3 of the mean internal energy density (**Exercise**: what is it in an isotropic 2D system?). This relationship between pressure and the energy of the particles makes physical sense: pressure is to do with how vigorously particles bombard the wall and that depends on how fast they are, on average.

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How large are the particle velocities? In view of the expression (1.29) for pressure, we can relate them to a macroscopic quantity that you might have encountered before: the sound speed in a medium of pressure $P$ and mass density $\rho = mn$ is (omitting constants of order unity) $c_\mathrm{s} \sim \sqrt{P/\rho} \sim \langle v^2\rangle^{1/2} \sim 300$ m/s [cf. (2.17)].

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For future use, let us see what isotropy implies for the pdf. Obviously, $f$ in an isotropic system must be independent of the direction of $\boldsymbol{v}$, it is a function of the *speed* $v = |\boldsymbol{v}|$ alone:

$$f(\boldsymbol{v}) = f(v). \tag{1.30}$$

This amounts to the system being spherically symmetric in $\boldsymbol{v}$ space, so it is convenient to change the $\boldsymbol{v}$-space variables to polar coordinates (Fig. 4):

$$(v_x, v_y, v_z) \to (v, \theta, \phi). \tag{1.31}$$

If we know $f(v_x, v_y, v_z)$, what is the joint pdf of $v$, $\theta$, $\phi$, which I will denote $\tilde{f}(v, \theta, \phi)$?

[9] This raises the interesting possibility that pressure need not, in general, be the same in all directions—a possibility that I will eliminate under the additional assumptions of §1.5, but resurrect in Exercise 1.4.

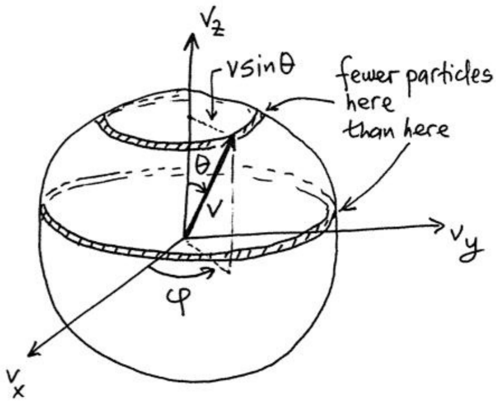


FIGURE 4. Polar coordinates in velocity space. The factor of $\sin\theta$ in (1.33) accounts for the fact that, if the particles are uniformly distributed over a sphere $|\boldsymbol{v}| = v$, there will be fewer of them in azimuthal bands at low $\theta$ than at high $\theta$ (the radius of an azimuthal band is $v\sin\theta$).

Here is how pdfs transform under change of variables:

$$f(\boldsymbol{v})\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z = \underbrace{f(\boldsymbol{v})\underbrace{\left|\frac{\partial(v_x, v_y, v_z)}{\partial(v,\theta,\phi)}\right|}_{\text{Jacobian}}}_{\tilde{f}(v,\theta,\phi)}\mathrm{d}v\mathrm{d}\theta\mathrm{d}\phi = f(\boldsymbol{v})v^2\sin\theta\,\mathrm{d}v\mathrm{d}\theta\mathrm{d}\phi. \tag{1.32}$$

Thus,

$$\tilde{f}(v,\theta,\phi) = f(\boldsymbol{v})v^2\sin\theta = f(v)v^2\sin\theta. \tag{1.33}$$

The last equality is a consequence of isotropy (1.30). It implies that an isotropic distribution of particle velocities is uniform in $\phi$, but not in $\theta$, and the pdf of particle speeds is[10]

$$\boxed{\tilde{f}(v) = \int_0^\pi \mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi\,\tilde{f}(v,\theta,\phi) = 4\pi v^2 f(v)}\,. \tag{1.34}$$

As an exercise in ascertaining the consistency of our formalism, let us calculate pressure again using polar coordinates in the velocity space (such calculations will prove useful later): as $v_z = v\cos\theta$,

$$\begin{aligned} P = mn\langle v_z^2\rangle &= mn\int \mathrm{d}^3\boldsymbol{v}\,v_z^2 f(\boldsymbol{v}) = mn\int_0^{2\pi}\mathrm{d}\phi\int_0^\pi \mathrm{d}\theta\sin\theta\cos^2\theta\int_0^\infty \mathrm{d}v\,v^4 f(v) \\ &= \frac{4\pi}{3}mn\int_0^\infty \mathrm{d}v\,v^4 f(v) = \frac{1}{3}mn\int_0^\infty \mathrm{d}v\,v^2\tilde{f}(v) = \frac{1}{3}mn\langle v^2\rangle, \end{aligned} \tag{1.35}$$

same as (1.29).

---

**Exercise 1.3.** (a) Prove, using $v_x = v\cos\phi\sin\theta$, $v_y = v\sin\phi\sin\theta$ and directly calculating integrals in $\boldsymbol{v}$-space polar coordinates, that

$$\langle v_x^2\rangle = \langle v_y^2\rangle = \frac{1}{3}\langle v^2\rangle. \tag{1.36}$$

[10] Blundell & Blundell (2009) call the distribution of speeds $f$ and the distribution of vector velocities $g$, so my $f$ is their $g$ and my $\tilde{f}$ is their $f$. This variation in notation should help you keep alert and avoid mechanical copying of formulae from textbooks.

(b) Calculate also $\langle v_x v_y \rangle$, $\langle v_x v_z \rangle$, $\langle v_y v_z \rangle$. Could you have worked out the outcome of this last calculation from symmetry arguments?

The answer to the last question is yes. Here is a smart way of computing $\langle v_i v_j \rangle$, where $i, j = x, y, z$ (in fact, you can do all this not just in 3D, but in any number of dimensions, $i, j = 1, 2, \dots, d$). Clearly, $\langle v_i v_j \rangle$ is a symmetric rank-2 tensor (i.e., a tensor, or matrix, with two indices, that remains the same if these indices are swapped). Since the velocity distribution is isotropic, this tensor must be rotationally invariant (i.e., not change under rotations of the coordinate frame). The only symmetric rank-2 tensor that has this property is the Kronecker delta $\delta_{ij}$ times a constant. So it must be the case that

$$\langle v_i v_j \rangle = C\delta_{ij}, \tag{1.37}$$

where $C$ can only depend on the distribution of *speeds* $v$ (not vectors $\boldsymbol{v}$). Work out what $C$ is. Is it the same in 2D and in 3D? This is a much simpler derivation than doing velocity integrals directly, but it was worth checking the result by direct integration, as you did above, to convince yourself that the symmetry magic works.

(c$^*$) Now that you know that it works, calculate $\langle v_i v_j v_k v_l \rangle$ in terms of averages of moments of $v$ (i.e., averages of powers of $v$ such as $\langle v^2 \rangle$ or $\langle v^4 \rangle$). *Hint.* Doing this by direct integration would be *a lot* of work. Generalise the symmetry argument given above: see what symmetric rotationally invariant rank-4 tensors (i.e., tensors with 4 indices) you can cook up: it will turn out that they have to be products of Kronecker deltas, e.g., $\delta_{ij}\delta_{kl}$; what other combinations are there? Then $\langle v_i v_j v_k v_l \rangle$ must be a linear combination of these tensors, with coefficients that depend on moments of $v$. By examining the symmetry properties of $\langle v_i v_j v_k v_l \rangle$, work out what these coefficients are. How does the answer depend on the dimensionality of the world (2D, 3D, $d$D)?

**Exercise 1.4.** Consider an *anisotropic* system, where there exists one (and only one) special direction in space (call it $z$) that affects the distribution of particle velocities (an example of such a situation is a gas of charged particles—plasma—in a straight magnetic field along $z$; see Schekochihin 2025, Part IV).

(a) How many variables does the velocity distribution function now depend on? (Recall that in the isotropic case, it depended only on one, $v$.) Write down the most general form of the distribution function under these symmetries—what is the appropriate transformation of variables from $(v_x, v_y, v_z)$?

(b) In terms of averages of these new velocity variables, what is the expression for the pressure $P_\parallel$ that the gas will exert on a wall perpendicular to the $z$ axis? (It is called $P_\parallel$ because it is due to particles whose velocities have non-zero projections onto the special direction $z$.) What is $P_\perp$, the pressure on any wall parallel to $z$?

(c) Now consider a wall the normal to which, $\hat{\boldsymbol{n}}$, is at an angle $\theta$ to $z$. What is the pressure on this wall in terms of $P_\parallel$ and $P_\perp$?

**Exercise 1.5.** Consider an insulated cylindrical vessel filled with monatomic ideal gas. The cylinder is closed on one side and plugged by a piston on the other side. The piston is very slowly pulled out (its velocity $u$ is much smaller than the typical velocities of the gas molecules). Show *using kinetic theory, not thermodynamics,* that during this process the pressure $P$ and volume $V$ of the gas inside the vessel are related by $PV^{5/3}$ =const. *Hint.* Consider how the energy of a gas particle changes after each collision with the piston and hence calculate the rate of change of the internal energy of the gas inside the vessel.

[Ginzburg *et al.* 2006, #307]

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## 2. Classical Ideal Gas in Equilibrium

I shall now introduce the simplest possible model of a gas and construct its pdf. The assumptions of the model are

- *Particles do not interact* (e.g., they do not attract or repel each other), except for having *elastic* binary collisions, during which they conserve total momentum and energy, do not fracture or stick.

• They are *point particles*, i.e., they do not occupy a significant fraction of the system's volume, however many of them there are. This assumption is necessary to ensure that a particle's ability to be anywhere in space is not restricted by being crowded out by other particles. This assumption will be relaxed for *"real gases"* in Part VII.

• They are *classical particles*, so there are *no quantum correlations* (which would jeopardise a particle's ability to have a particular momentum if the corresponding quantum state is already occupied by another particle). We will relax this assumption for *"quantum gases"* in Part VI.

• They are *non-relativistic particles*, i.e., their speeds are $v \ll c$. You will have an opportunity to play around with relativistic gases later on (e.g., Exercise 11.4).

In practice, all this is satisfied if the gas is sufficiently *dilute* (low enough number density $n$) and sufficiently *hot* (high enough temperature $T$) to avoid Quantum Mechanics, but not so hot as to run into Relativity. I will make these constraints quantitative after I define $T$ (see §2.3).

## 2.1. *Maxwell's Distribution*

[Literature: Pauli (2003), §25]

Consider our model gas in a container of volume $V$ and assume that there are no changes to external (boundary) conditions or fields—everything is *homogeneous in time and space.*

Let us wait long enough for a sufficient number (=a few) of *collisions* to occur so *all memory of initial conditions is lost* (recall the discussion in §1.1 of how that happens; roughly how long we must wait we will be able to estimate after we discuss collisions in §4).

We shall call the resulting state an *equilibrium* in the sense that it will be *statistically stationary*, i.e., the particles in the gas will settle into some *velocity distribution independent of time, position or initial conditions* (NB: it is essential to have collisions to achieve this!). How the gas attains such a state will be the subject of §§5–6.

Since the distribution function $f(\boldsymbol{v})$ does not depend on anything, we must be able to work out what it is from some general principles.

First of all, if there are *no special directions* in the system, the pdf must be isotropic [see (1.30)]:

$$f(\boldsymbol{v}) = f(v) = g(v^2), \tag{2.1}$$

where $g$ is some function of $v^2$ (introduced for the convenience of the upcoming derivation).

---

**Exercise 2.1.** In the real world, you might object, there are always special directions. For example, gravity (particles have mass!). After we have finished deriving $f(v)$, think under what condition gravity can be ignored.

Also, the Earth is rotating in a definite direction, so particles in the atmosphere are subject to Coriolis and centrifugal forces. Under what condition can these forces be ignored?

---

Maxwell (1860) argued (or conjectured) that *the three components of the velocity vector* *must be independent random variables.*[11] Then

$$f(\boldsymbol{v}) = h(v_x^2)h(v_y^2)h(v_z^2), \tag{2.2}$$

where all three distributions are the same because of isotropy and depend only on squares of velocity components, assuming *mirror symmetry* of the distribution (invariance with respect to the transformation $\boldsymbol{v} \to -\boldsymbol{v}$; this means there are no flows or fluxes in the system).

But in view of isotropy (2.1), (2.2) implies

$$h(v_x^2)h(v_y^2)h(v_z^2) = g(v^2) = g(v_x^2 + v_y^2 + v_z^2). \tag{2.3}$$

Denoting further

$$\varphi(v_x^2) \equiv \ln h(v_x^2) \quad \text{and} \quad \psi(v^2) \equiv \ln g(v^2), \tag{2.4}$$

we find

$$\varphi(v_x^2) + \varphi(v_y^2) + \varphi(v_z^2) = \psi(v_x^2 + v_y^2 + v_z^2). \tag{2.5}$$

Such a functional relationship can only be satisfied if $\varphi$ and $\psi$ are *linear functions* of their arguments:

$$\varphi(v_x^2) = -\alpha v_x^2 + \beta \quad \text{and} \quad \psi(v^2) = -\alpha v^2 + 3\beta. \tag{2.6}$$

Here $\alpha$ and $\beta$ are as yet undetermined integration constants and the minus sign is purely a matter convention ($\alpha$ will turn out to be positive).

---

**Proof.** Differentiate (2.5) with respect to $v_x^2$ keeping $v_y^2$ and $v_z^2$ constant:

$$\psi'(v_x^2 + v_y^2 + v_z^2) = \varphi'(v_x^2). \tag{2.7}$$

Differentiate this again with respect to $v_y^2$ keeping $v_x^2$ and $v_z^2$ constant:

$$\psi''(v_x^2 + v_y^2 + v_z^2) = 0, \quad \text{or} \quad \psi''(v^2) = 0. \tag{2.8}$$

Therefore,

$$\psi(v^2) = -\alpha v^2 + 3\beta, \tag{2.9}$$

where $-\alpha$ and $3\beta$ are constants of integration. This is the desired solution (2.6) for $\psi$.

Now substitute this form of $\psi$ into (2.5) and let $v_y^2 = v_z^2 = 0$:

$$\varphi(v_x^2) + 2\varphi(0) = \psi(v_x^2) = -\alpha v_x^2 + 3\beta. \tag{2.10}$$

Let $v_x^2 = 0$ in the above: this gives $\varphi(0) = \beta$. Then (2.10) becomes

$$\varphi(v_x^2) = -\alpha v_x^2 + \beta, \quad \text{q.e.d.} \tag{2.11}$$

---

From (2.6), we deduce immediately that

$$f(\boldsymbol{v}) = g(v^2) = e^{\psi(v^2)} = C\, e^{-\alpha v^2}, \quad \text{where} \quad C \equiv e^{3\beta}, \tag{2.12}$$

so the velocity distribution has a Gaussian ("bell-curve") shape. It remains to determine the constants $\alpha$ and $C$. One of them is easy: we know that $\int \mathrm{d}^3\boldsymbol{v}\, f(\boldsymbol{v}) = 1$, so

$$1 = C\int \mathrm{d}^3\boldsymbol{v}\, e^{-\alpha v^2} = C\int \mathrm{d}v_x e^{-\alpha v_x^2}\int \mathrm{d}v_y e^{-\alpha v_y^2}\int \mathrm{d}v_z e^{-\alpha v_z^2} = C\left(\sqrt{\frac{\pi}{\alpha}}\right)^3. \tag{2.13}$$

[11] It is possible to prove this for classical ideal gas either from Statistical Mechanics (see §11.11) or by analysing elastic binary collisions (Boltzmann 1995; Chapman & Cowling 1991), but here we will simply *assume* that this is true.

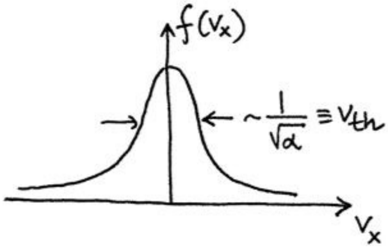


FIGURE 5. The Maxwellian distribution (2.14).

Therefore,

$$C = \left(\frac{\alpha}{\pi}\right)^{3/2} \quad\Rightarrow\quad f(\boldsymbol{v}) = \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha v^2}. \tag{2.14}$$

Thus, we have expressed $f(\boldsymbol{v})$ in terms of only one scalar parameter $\alpha$! Have we derived something from nothing? Not quite: the functional form of the pdf followed from a set of assumptions about (statistical) *symmetries* of the equilibrium state.

What is the meaning of $\alpha$? This parameter tells us about the *width* of the velocity distribution (Fig. 5). Dimensionally, $1/\sqrt{\alpha} = v_{\rm th}$ is some characteristic speed, which we call the *thermal speed* (formally, this is just a renaming, but it helps interpretation). It characterises the typical values that particle velocities can take (having $v \gg v_{\rm th}$ is highly improbable because of the strong decay of the Gaussian function). With this new notation, we have

$$\boxed{f(\boldsymbol{v}) = \frac{1}{(\sqrt{\pi}v_{\rm th})^3}\, e^{-v^2/v_{\rm th}^2}}\,, \tag{2.15}$$

an easy-to-remember functional form. This will be called *Maxwell's distribution*, also known as a *Maxwellian*, once we manage to give thermodynamical interpretation to $v_{\rm th}$ (see §2.2).

To complete the formalism, the pdf of speeds is [see (1.34)]

$$\tilde{f}(v) = \frac{4\pi v^2}{(\sqrt{\pi}v_{\rm th})^3}\, e^{-v^2/v_{\rm th}^2}. \tag{2.16}$$

Note that $v_{\rm th}$ is the most probable speed (Fig. 6; **Exercise**: prove this).

---

It is claimed (by Kapitsa 1974) that the problem to find the distribution of particle velocities in a gas was routinely set by Stokes at a graduate exam in Cambridge in mid-19th century—the answer was unknown and Stokes' purpose was to check whether the examinee had the erudition to realise this. To Stokes' astonishment, a student called James Clerk Maxwell solved the problem during his exam.

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All these manipulations are well and good, but to relate $v_{\rm th}$ to something physical, we need to relate it to something *measurable*. What is measurable about a gas in a box? The two most obviously measurable quantities are

—pressure (we can measure force on a wall),

—temperature (we can stick in a thermometer, as it is defined in Thermodynamics).

We will see in the next section how to relate $v_{\rm th}$, $T$ and $P$.

---

**Exercise 2.2.** (a) Work out a general formula for $\langle v^n\rangle$ ($n$ is an arbitrary positive integer) in terms of $v_{\rm th}$, for a Maxwellian gas (*hint:* it is useful to consider separately odd and even $n$). If $n < m$, what is larger, $\langle v^n\rangle^{1/n}$ or $\langle v^m\rangle^{1/m}$? Why is this, qualitatively?

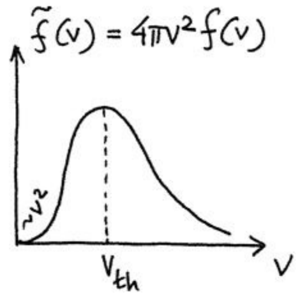


FIGURE 6. The pdf of speeds for a Maxwellian distribution (2.16).

(b*) What is the distribution of speeds $\tilde{f}(v)$ in a Maxwellian $d$-dimensional gas? *Hint.* This involves calculating the area of a $d$-dimensional unit sphere in velocity space.

(c) Obtain the exact formula for the rms energy fluctuation in a Maxwellian gas (see §1.3).

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### 2.2. *Equation of State and Temperature*

In §1, we learned how, given $f(\boldsymbol{v})$, to compute pressure: the Maxwellian (2.15) is isotropic, so, using (1.35),

$$P = \frac{1}{3}mn\langle v^2\rangle = \frac{1}{3}mn\int d^3\boldsymbol{v}\, v^2 \frac{e^{-v^2/v_{\rm th}^2}}{(\sqrt{\pi}v_{\rm th})^3} = \frac{nmv_{\rm th}^2}{2} \quad\Rightarrow\quad \boxed{v_{\rm th} = \sqrt{\frac{2P}{nm}}}\,. \tag{2.17}$$

This provides us with a clear relationship between $v_{\rm th}$ and the thermodynamic quantities $P$ and $n = N/V$. Furthermore, we know empirically[12] that, for 1 mole of ideal gas ($N = N_{\rm A} = 6.022140857 \times 10^{23}$, the Avogadro number of particles),

$$PV = RT, \quad \text{where} \quad R = 8.31447\ \text{J/K} \quad (\text{the } \textit{gas constant}), \tag{2.18}$$

and $T$ is the absolute temperature as defined in Thermodynamics (via Zeroth Law etc.; see Part I). Another, equivalent, form of this *equation of state* is

$$P = nk_{\rm B}T, \quad \text{where} \quad k_{\rm B} = \frac{R}{N_{\rm A}} = 1.3807\times 10^{-23}\ \text{J/K} \quad (\text{the } \textit{Boltzmann constant}). \tag{2.19}$$

Comparing (2.19) and (2.17), we can extract the relationship between $v_{\rm th}$ and the thermodynamic temperature:

$$\boxed{\frac{mv_{\rm th}^2}{2} = k_{\rm B}T}\,. \tag{2.20}$$

Thus, *temperature in Kinetic Theory is simply the kinetic energy of a particle moving at the most probable speed in the Maxwellian velocity distribution,*[13] or, vice versa, the

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[12]From the thermodynamic experiments of Boyle 1662, Mariotte 1676 ($P \propto 1/V$ at constant $T$), Charles 1787 ($V \propto T$ at constant $P$), Gay-Lussac 1809 ($P \propto T$ at constant $V$) and Amontons 1699 (who anticipated the latter two by about a century). To be precise, what we know empirically is that (2.18) holds for the thermodynamically defined quantities $P$ and $T$ in most gases as long as they are measured in parameter regimes in which we expect the ideal gas approximation to hold.

[13]The Boltzmann constant $k_{\rm B}$ is just a dimensional conversion coefficient owing its existence to the fact that historically $T$ is measured in $K$ rather than in units of energy (as it should have been).

width of the Maxwellian is related to temperature via

$$v_{\rm th} = \sqrt{\frac{2k_{\rm B}T}{m}}. \tag{2.21}$$

Two other, equivalent, statements of this sort are that (**Exercise**: prove them)

$$\frac{1}{2}\,k_{\rm B}T = \frac{m\langle v_x^2\rangle}{2}, \tag{2.22}$$

the mean energy per particle per degree of freedom, and, recalling the definition (1.10) of $U$, that

$$\frac{3}{2}\,k_{\rm B}T = \frac{U}{N}, \tag{2.23}$$

the mean energy per particle.[14] From (2.23), *the heat capacity* of monatomic classical ideal gas is

$$C_V = \frac{3}{2}\,k_{\rm B}N. \tag{2.24}$$

Finally, using our expression (2.21) for $v_{\rm th}$, we arrive at the traditional formula for the Maxwellian: (2.15) becomes

$$\boxed{f(\boldsymbol{v}) = \left(\frac{m}{2\pi k_{\rm B}T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_{\rm B}T}\right)}\,. \tag{2.25}$$

This is a particular case (which we have here derived for our model gas) of a much more general statistical-mechanical result known as the Gibbs distribution—exactly how to recover Maxwell from Gibbs will be explained in §11.11.

The above treatment has not just given us the particle-velocity pdf in equilibrium—we have also learned something new and important about the physical meaning of temperature, *which has turned out to measure how energetic, on average, microscopic particles are*. This is progress compared to Thermodynamics, where $T$ was a purely macroscopic and rather mysterious (if indispensable) quantity: recall that the defining property of $T$ was that it was some quantity that would equalise across a system in equilibrium (e.g., if two systems with initially different temperatures were brought into contact); in Thermodynamics, we were able to prove that such a quantity must exist, but we could not explain exactly what it was or how the equalisation happened. It is now clear how it happens for two volumes of gas when they are mixed together: particles collide and eventually attain a global Maxwellian distribution with a single parameter $\alpha \Leftrightarrow v_{\rm th} \Leftrightarrow T$. When the gas touches a hot or cold wall, particles of the gas collide with the vibrating molecules of the wall—the energy of this vibration is also proportional to $T$, as we will see in Statistical Mechanics—and again attain a Maxwellian with the same $T$.

To summarise, we now have the full *thermodynamics of classical monatomic ideal gas:* specific formulae (2.23) for energy $U = U(N,T)$, (2.24) for heat capacity $C_V = C_V(N)$, (2.19) for the equation of state $P = P(N,V,T)$, etc. In addition, we know the full velocity distribution (2.25), and so can calculate other interesting things, which thermodynamics is ignorant of (effusion, §3, will be the first example of that, followed by the great and glorious theory of heat and momentum transport, §§5–6).

[14] Note that one sometimes *defines* temperature in Kinetic Theory via (2.23), (2.22) or (2.20) and then proves the equivalence of this "kinetic temperature" and the thermodynamic temperature (see, e.g., Chapman & Cowling 1991).

### 2.3. *Validity of the Classical Limit*

Here are two very quick estimates for the range of temperatures in which the classical results derived above should hold.

#### 2.3.1. *Nonrelativistic Limit*

Particles must be much slower than light:

$$k_B T = \frac{m v_{\rm th}^2}{2} \ll mc^2 \quad \Rightarrow \quad T \ll \frac{mc^2}{k_B} \equiv T_{\rm rel}. \tag{2.26}$$

If we formally substitute into this formula the typical molecular mass for air, we get $T_{\rm rel} \sim 10^{14}$ K (but of course molecules will have dissociated and atoms have become ionised at much lower temperatures than this). This being a huge number tells us that working in the non-relativistic limit is very safe.

#### 2.3.2. *No Quantum Correlations*

We are thinking of particles as hard point spheres whizzing about with certain velocities and occasionally colliding. But in quantum mechanics, if a particle has a definite velocity (momentum), it cannot have a definite position, so certainly cannot be thought of as a "point." The relationship between the uncertainties in the particle momentum and its position is

$$\delta r \delta p \sim \hbar. \tag{2.27}$$

Let us estimate the momentum uncertainty as the thermal spread in the particle velocity distribution:

$$\delta p \sim m v_{\rm th} \sim \sqrt{m k_B T}. \tag{2.28}$$

Then we can continue thinking of particles as points if the typical extent of the volume of space per particle $(1/n)$ is much larger than the uncertainty in the particle's position:[15]

$$\frac{1}{n^{1/3}} \gg \delta r \sim \frac{\hbar}{\delta p} \sim \frac{\hbar}{m v_{\rm th}} \sim \frac{\hbar}{\sqrt{m k_B T}} \quad \Rightarrow \quad T \gg \frac{\hbar^2 n^{2/3}}{m k_B} \equiv T_{\rm deg}. \tag{2.29}$$

The "degeneration temperature" $T_{\rm deg}$ for air at $P = 1$ atm is a few K, but of course most gases will liquefy or even solidify at such temperatures. Again, we see that the classical approximation appears to be quite safe for our current, mundane purposes. Note, however, that $T_{\rm deg}$ depends on density (or pressure, $P = n k_B T$), and when this is very high, gas can become quantum even at quite high temperatures (a famous example is electrons in metals)—then particles get "smeared" over each other and one has to worry about quantum correlations. We shall do this in Part VI.

## 3. Effusion

Let us practice our newly acquired knowledge of particle distributions (§2) and calculations of fluxes (§1.4) on a simple, but interesting, problem.

Consider a container containing ideal gas and make a small hole in it (Fig. 7). Suppose the hole is so small that its diameter

$$d \ll \lambda_{\rm mfp}, \tag{3.1}$$

where $\lambda_{\rm mfp}$ is the particle mean free path (the typical distance that particles travel between collisions—we will calculate it in §4). Then macroscopically the gas does not

[15] Another way to get this is to demand that the volume per particle should contain many de Broglie wave lengths $\lambda_{\rm dB} = h/p$ associated with the thermal motion: $n\lambda_{\rm dB}^3 \sim n(h/m v_{\rm th})^3 \ll 1$.

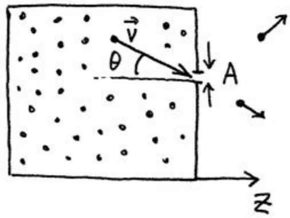


FIGURE 7. Effusion: gas escapes from a container through a small hole.

"know" about the hole—this is a way to abduct particles without changing their distribution.[16] This can be a way to find out, non-invasively, what the velocity distribution is inside the container, provided we have a way of measuring the velocities of the escaping particles. On an even more applied note, we might be interested in what happens in this set up because we are concerned about gas leaks through small holes in some industrially important walls or partitions.

There are two obviously interesting quantitative questions that we can ask:

(i) Given some distribution of particles inside the container, $f(\boldsymbol{v})$, what will be the distribution of the particles emerging from the hole?

(ii) Given the area $A$ of the hole, how many particles escape through it per unit time? (i.e., what is the particle *flux* through the hole?)

The answers are quite easy to obtain. Indeed, this is just like the calculation of pressure (§1.4): there we needed to calculate the flux of momentum carried by the particles hitting an area of the wall; here we need the flux of particles themselves that hit an area of the wall (hole of area $A$)—these particles will obviously be the ones that escape through the hole. Taking, as in §1.4, $z$ to be the direction perpendicular to the wall, we find that the (differential) particle flux, i.e., the number per unit time per unit area of particles with velocities in the 3D cube $[\boldsymbol{v}, \boldsymbol{v} + \mathrm{d}^3\boldsymbol{v}]$, is [see (1.21)]

$$\mathrm{d}\Phi(\boldsymbol{v}) = n v_z f(\boldsymbol{v})\,\mathrm{d}^3\boldsymbol{v} = n \underbrace{v^3 f(v)\mathrm{d}v}_{\substack{\text{speed dis-}\\ \text{tribution}}} \underbrace{\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}_{\substack{\text{angular}\\ \text{distribution}}}, \tag{3.2}$$

where, in the second expression, we assumed that the distribution is isotropic, $f(\boldsymbol{v}) = f(v)$, and used $v_z = v\cos\theta$ and $\mathrm{d}^3\boldsymbol{v} = v^2\sin\theta\,\mathrm{d}v\,\mathrm{d}\theta\,\mathrm{d}\phi$.

Thus, we have the answer to our question (i) and conclude that *the distribution of the emerging particles is neither isotropic nor Maxwellian* (even if the gas inside the container is Maxwellian). The angle distribution is not isotropic (has an extra $\cos\theta$ factor) because particles travelling nearly perpendicularly to the wall (small $\theta$) escape with greater probability.[17] The speed distribution is not Maxwellian (has an extra factor of $v$; Fig. 8) because faster particles get out with greater probability (somewhat like the smarter students passing with greater probability through the narrow admissions filter into Oxford—not an entirely deterministic process though, just like effusion).

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[16] In §5, we will learn what happens when the gas does "know" and why the hole has to be larger than $\lambda_{\mathrm{mfp}}$ for that.

[17] However, there are fewer of these particles in the original isotropic angle distribution $\propto \sin\theta\mathrm{d}\theta\mathrm{d}\phi$, so statistically, it is $\theta = 45^\circ$ that is the most probable angle for the effusing particles.

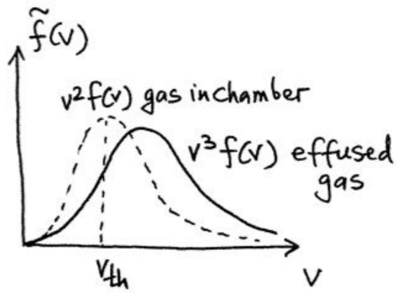


FIGURE 8. Speed distribution of effusing particles: favours faster particles more than the Maxwellian; see (3.3).

**Exercise 3.1.** (a) Consider a gas effusing out through a small hole into an evacuated sphere, with the particles sticking to the internal surface of the sphere once they hit it. Show that this would produce a uniform coating of the surface.

(b) Show that the distribution of the speeds of the particles that might be found in transit between the effusion hole and the surface at any given time is the same as for a Maxwellian gas.

---

If we are only interested in the distribution of speeds, we can integrate out the angular dependence in (3.2): the flux through the hole of particles with *speeds* in the interval $[v, v + \mathrm{d}v]$ is

$$\mathrm{d}\tilde{\varPhi}(v) = nv^3 f(v)\mathrm{d}v \int_0^{\pi/2} \mathrm{d}\theta\, \cos\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi = \pi n v^3 f(v)\mathrm{d}v = \frac{1}{4}\, nv\tilde{f}(v)\mathrm{d}v, \tag{3.3}$$

where $\tilde{f}(v)$ is the distribution of speeds inside the container, related to $f(v)$ via (1.34). Note the upper limit of integration with respect to $\theta$: it is $\pi/2$ and not $\pi$ because only particles moving *toward* the hole ($v_z = v\cos\theta > 0$) will escape through it.

Finally, the total flux of effusing particles (number of particles per unit time per unit area escaping through the hole, no matter what their speed) is

$$\varPhi = \int_0^\infty \mathrm{d}v\, \frac{1}{4}\, nv\tilde{f}(v) = \frac{1}{4}\, n\langle v\rangle, \tag{3.4}$$

where $\langle v\rangle$ is the average particle speed inside the container. For a Maxwellian distribution, $\tilde{f}(v)$ is given by (2.16) and so $\langle v\rangle$ can be readily computed:

$$\boxed{\varPhi = \frac{1}{4}\, n\sqrt{\frac{8k_\mathrm{B}T}{\pi m}} = \frac{P}{\sqrt{2\pi m k_\mathrm{B}T}}} \tag{3.5}$$

(**Exercise**: check this result; use the ideal-gas equation of state).

Thus, we have the answer to our question (ii): the number of particles effusing per unit time through a hole of area $A$ is $\varPhi A$, viz.,

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\varPhi A, \tag{3.6}$$

where $\varPhi$ can be calculated via (3.5) in terms of macroscopic measurable quantities, $P$ (or $n$) and $T$, if we know the mass $m$ of the particles.

---

The fact that, given $P$ and $T$, the effusion flux $\varPhi \propto m^{-1/2}$, implies that if we put a mixture of two particle species into a box with a small hole and let them effuse, the lighter species will effuse at a larger rate than the heavier one, so the composition of the blend emerging on the

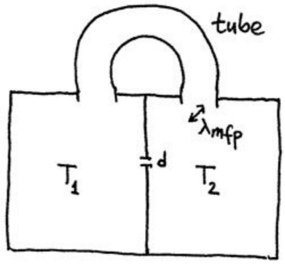


FIGURE 9. Two chambers connected by a tube or an effusion hole (Exercise 3.6).

other side of the hole will favour the lighter particles. This has applications to separation of isotopes. These applications are strictly on a need-to-know basis.

---

**Exercise 3.2.** Show that the condition of no mass flow between two insulated chambers containing ideal gas at pressures $P_{1,2}$ and temperatures $T_{1,2}$ and connected by a tiny hole is

$$\frac{P_1}{\sqrt{T_1}} = \frac{P_2}{\sqrt{T_2}}. \tag{3.7}$$

What would be the condition for no flow if the hole between the chambers were large ($d \gg \lambda_{\rm mfp}$)?

**Exercise 3.3.** What is the *energy flux* through the hole? (i.e., what is the energy lost by the gas in the container per unit time, as particles leave by a hole of area $A$?)

**Exercise 3.4.** Consider a thermally insulated container of volume $V$ with a small hole of area $A$, containing a gas with molecular mass $m$. At time $t = 0$, the density is $n_0$ and the temperature is $T_0$. As gas effuses out through a small hole, both density and temperature inside the container will drop. Work out their time dependence, $n(t)$ and $T(t)$, in terms of the quantities given above. What is the characteristic time over which they will change significantly? *Hint.* Temperature is related to the total energy of the particles in the container. The flux of energy of the effusing particles will determine the rate of change of energy inside the container in the same way as the particle flux determines the rate of change of the particle number (and, therefore, their density). Based on this principle, you should be able to derive two differential (with respect to time) equations for two unknowns, $n$ and $T$. Having derived them, solve them.

**Exercise 3.5.** A festive helium balloon of radius $R = 20$ cm made of a soft but unstretchable material is tied to a lamppost in Oxford High Street. The material is not perfect and can have microholes of approximate radius $r = 10^{-5}$ cm, through which helium will be leaking out. As this happens, the balloon shrinks under atmospheric pressure.

(a) Assuming the balloon material is a good thermal conductor, calculate how many microholes per cm$^2$ the balloon can have if it is to lose no more than 10% of its initial volume over one festive week.

(b) Now suppose the balloon material is a perfect thermal insulator. Repeat the calculation.

**Exercise 3.6.** Consider two chambers of equal volume separated by an insulating wall and containing an ideal gas maintained at two distinct temperatures $T_1 < T_2$. Initially the chambers are connected by a long tube (Fig. 9) whose diameter is much larger than the mean free path in either chamber, and equilibrium is established (while maintaining $T_1$ and $T_2$). Then the tube is removed, the chambers are sealed, but a small hole is opened in the insulating wall, with diameter $d \ll \lambda_{\rm mfp}$ (where the mean free path is for either gas).

(a) In what direction will the gas flow through the hole, from cold to hot or from hot to cold?

(b) If the total mass of the gas in both chambers is $M$, show that the mass $\Delta M$ transferred through the hole from one chamber to the other before a new equilibrium is established is

$$\Delta M = \frac{\sqrt{T_1 T_2}}{T_1 + T_2} \frac{\sqrt{T_2} - \sqrt{T_1}}{\sqrt{T_1} + \sqrt{T_2}} M. \tag{3.8}$$

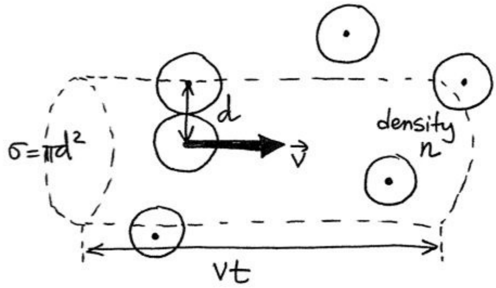


FIGURE 10. Cross section, collision time and mean free path.

[Ginzburg *et al.* 2006, #427]

## 4. Collisions

We argued (on plausible symmetry grounds) that in equilibrium, we should expect the pdf to be Maxwellian for an ideal gas. "In equilibrium" meant that initial conditions were forgotten, i.e., that particles had collided a sufficient number of times. There are certain constraints on the time scales on which the gas is likely to be in equilibrium (how long do we wait for the gas to "Maxwellianise"?) and on the spatial scales of the system if we are to describe it in these terms. Namely,

- $t \gg \tau_c$, the *collision time*, or the typical time that a particle spends in free flight between collisions (it is also convenient to define the *collision rate* $\nu_c = 1/\tau_c$, the typical number of collisions a particle has per unit time);
- $l \gg \lambda_{mfp}$, the *mean free path*, or the typical distance a particle travels between collisions.

In order to estimate $\tau_c$ and $\lambda_{mfp}$, we will have to bring in some information and some assumptions about the microscopic properties of the gas and the nature of collisions.

### 4.1. *Cross-section*

Assume that particles are *hard spheres* of diameter $d$. Then they can be considered to collide if their centres approach each other within the distance $d$. Think of a particle with velocity $\boldsymbol{v}$ moving through a cylinder (Fig. 10) whose axis is along $\boldsymbol{v}$ and whose cross section is

$$\sigma = \pi d^2. \tag{4.1}$$

As the particle will necessarily collide with any other particle whose centre is within this cylinder, $\sigma$ is called the *collisional cross section.*

A useful way of parametrising the more general situation in which particles are *not* hard spheres but instead interact with each other via some smooth potential (e.g., charged particles feeling each other's Coulomb potential), is to introduce the "effective cross section," in which case $d$ tells you how close they have to get to have a "collision," i.e., to be significantly deflected from a straight path.

**Exercise 4.1. Coulomb Collisions.** For particles with charge $e$, mass $m$ and temperature $T$, estimate $d$.

## 4.2. *Collision Time*

Moving through the imaginary cylinder of cross section $\sigma$, a particle sweeps the volume $\sigma v t$ over time $t$. The average number of other particles in this volume is $\sigma v t n$. If this is $> 1$, then there will be at least one collision during the time $t$. Thus, we define the *collision time* $t = \tau_c$ so that

$$\sigma v \tau_c n = 1 \quad \Rightarrow \quad \tau_c = \frac{1}{\sigma n v}, \quad \nu_c = \frac{1}{\tau_c} = \sigma n v. \tag{4.2}$$

As we are interested in a "typical" particle, $v$ here is some typical speed. For a Maxwellian distribution, we may pick any of these:

$$v \sim \langle v \rangle \sim v_{\rm rms} \sim v_{\rm th}. \tag{4.3}$$

All these speeds have different numerical coefficients (viz., $\langle v \rangle = 2v_{\rm th}/\sqrt{\pi}$, $v_{\rm rms} = \sqrt{3/2}\, v_{\rm th}$), but we are in the realm of order-of-magnitude estimates here, so it does not really matter which we choose. To fix the notation, let us define

$$\boxed{\tau_c = \frac{1}{\nu_c} = \frac{1}{\sigma n v_{\rm th}} = \frac{1}{\sigma n}\sqrt{\frac{m}{2k_{\rm B}T}}}\,. \tag{4.4}$$

## 4.3. *Mean Free Path*

Then the typical distance a particle travels between collisions is

$$\boxed{\lambda_{\rm mfp} = v_{\rm th}\tau_c = \frac{1}{\sigma n}} \tag{4.5}$$

(or I could have said that this is the length of the cylinder of cross section $\sigma$ such that it contains at least one particle: $\sigma \lambda_{\rm mfp} n = 1$).

Note that, given the gas density, $\lambda_{\rm mfp}$ is independent of temperature. At constant $T$, it is $\lambda_{\rm mfp} = k_{\rm B}T/\sigma P \propto P^{-1}$, inversely proportional to pressure.

---

## 4.4. *Relative Speed*

[Literature: Pauli (2003), §26]

If you have a suspicious mind, you might worry that the arguments above are somewhat dodgy: indeed, we effectively assumed that while our chosen particle moved through its $\sigma v t$ cylinder, all other particles just sat there waiting to be collided with. Surely what matters is, in fact, the *relative* speed of colliding particles? This might prompt one to introduce the following definition for the mean collision rate, which is conventional:

$$\nu_c = \sigma n \langle v_r \rangle, \tag{4.6}$$

where $v_r = |\boldsymbol{v}_1 - \boldsymbol{v}_2|$ is the mean relative speed of a pair of particles. It is more or less obvious that $\langle v_r \rangle \sim v_{\rm th}$ just like any other speed in a Maxwellian distribution (what else could it possibly be?!), but let us convince ourselves of this anyway (it is also an instructive exercise to calculate $\langle v_r \rangle$).

By definition,

$$\langle v_r \rangle = \int d^3\boldsymbol{v}_1 \int d^3\boldsymbol{v}_2 |\boldsymbol{v}_1 - \boldsymbol{v}_2| f(\boldsymbol{v}_1, \boldsymbol{v}_2), \tag{4.7}$$

where $f(\boldsymbol{v}_1, \boldsymbol{v}_2)$ is the joint two-particle distribution function (i.e., the pdf that the first velocity is in a $d^3\boldsymbol{v}_1$ interval around $\boldsymbol{v}_1$ and the second in $d^3\boldsymbol{v}_2$ around $\boldsymbol{v}_2$). Now we make a key assumption:

$$f(\boldsymbol{v}_1, \boldsymbol{v}_2) = f(\boldsymbol{v}_1) f(\boldsymbol{v}_2), \tag{4.8}$$

i.e., the two particles' velocities are *independent*. This makes sense as long as we are considering them *before* they have undergone a collision—remember that particles are non-interacting in an ideal gas, except for collisions.[18] Taking the single-particle pdfs $f$ to be Maxwellian, one gets

$$\begin{aligned}\langle v_\mathrm{r}\rangle &= \int\int \mathrm{d}^3\boldsymbol{v}_1 \mathrm{d}^3\boldsymbol{v}_2 |\boldsymbol{v}_1 - \boldsymbol{v}_2| \frac{1}{(\pi v_\mathrm{th}^2)^3} \exp\left(-\frac{v_1^2}{v_\mathrm{th}^2} - \frac{v_2^2}{v_\mathrm{th}^2}\right) \\ &= \int \mathrm{d}^3\boldsymbol{v}_\mathrm{r} v_\mathrm{r} \int \mathrm{d}^3\boldsymbol{V} \frac{1}{(\pi v_\mathrm{th}^2)^3} \exp\left(-\frac{2V^2}{v_\mathrm{th}^2} - \frac{v_\mathrm{r}^2}{2v_\mathrm{th}^2}\right) \\ &= \int \mathrm{d}^3\boldsymbol{v}_\mathrm{r} v_\mathrm{r} \frac{1}{(\sqrt{2\pi} v_\mathrm{th})^3} \exp\left(-\frac{v_\mathrm{r}^2}{2v_\mathrm{th}^2}\right) = \sqrt{2}\langle v\rangle = \frac{2\sqrt{2}\, v_\mathrm{th}}{\sqrt{\pi}} = 4\sqrt{\frac{k_\mathrm{B}T}{\pi m}}. \end{aligned} \tag{4.9}$$

In the calculation of the double integral, I changed variables $(\boldsymbol{v}_1, \boldsymbol{v}_2) \to (\boldsymbol{V}, \boldsymbol{v}_\mathrm{r})$, where $\boldsymbol{V} = (\boldsymbol{v}_1 + \boldsymbol{v}_2)/2$ is the centre of mass and $\boldsymbol{v}_\mathrm{r} = \boldsymbol{v}_1 - \boldsymbol{v}_2$ the relative velocity; then $v_1^2 + v_2^2 = 2V^2 + v_\mathrm{r}^2/2$ and $\mathrm{d}^3\boldsymbol{v}_1\mathrm{d}^3\boldsymbol{v}_2 = \mathrm{d}^3\boldsymbol{V}\mathrm{d}^3\boldsymbol{v}_\mathrm{r}$.

It is in view of this result that some books define the mean collision rate

$$\nu_\mathrm{c} = \sqrt{2}\,\sigma n \langle v\rangle = \frac{1}{\tau_\mathrm{c}} \tag{4.10}$$

and the mean free path

$$\lambda_\mathrm{mfp} = \langle v\rangle \tau_\mathrm{c} = \frac{1}{\sqrt{2}\,\sigma n} \tag{4.11}$$

(here $\langle v\rangle$, *not* $\langle v_\mathrm{r}\rangle$, is used because $\lambda_\mathrm{mfp}$ is just the distance one particle travels at the average speed over time $\tau_\mathrm{c}$). Of course, these formulae in a sense represent precision overkill: $\nu_\mathrm{c}$ and $\lambda_\mathrm{mfp}$ are quantities whose purpose is order-of-magnitude estimate of the collisional time and spatial scales, so factors of order unity are irrelevant.

---

**Exercise 4.2.** Show that $\langle v_\mathrm{r}^2\rangle = 2\langle v^2\rangle$. *Hint.* This is much easier to show than $\langle v_\mathrm{r}\rangle = \sqrt{2}\langle v\rangle$. You should not need more than one line of trivial algebra to prove it.

**Exercise 4.3.** Consider a gas that is a mixture of two species of molecules: type-1 with diameter $d_1$, mass $m_1$ and mean number density $n_1$ and type-2 with diameter $d_2$, mass $m_2$ and mean number density $n_2$. If we let them collide with each other for a while, they will eventually settle into a Maxwellian equilibrium and the temperatures of the two species will be the same.

(a) What will be the rms speed of each of the two species?

(b) Show that the combined pressure of the mixture will be $P = P_1 + P_2$ (*Dalton's law*).

(c) What is the cross-section for the collisions between type-1 and type-2 molecules?

(d) What is the mean collision rate of type-1 molecules with type-2 molecules? Is it the same as the collision rate of type-2 molecules with type-1 molecules? (Think carefully about what exactly you mean when you define these rates.) *Hint.* You will need to find the mean relative speed of the two types of particles, a calculation analogous to the one in §4.4. Note however, that as the masses of the particles of the two different types can be very different, the distinction between $\langle v_\mathrm{r}\rangle$ and $\langle v_1\rangle$ or $\langle v_2\rangle$ can now be much more important than in the case of like-particle collisions.

(e) Work out the 1–2 and 2–1 collision rates in the limit $m_1 \gg m_2$. Interpret your results physically.

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## 5. From Local to Global Equilibrium (Transport Equations)

[18]It certainly would not be sensible to assume that they are independent right *after* a collision. The assumption of independence of particle velocities before a collision is a key one in the derivation of Boltzmann's collision integral (Boltzmann 1995; Chapman & Cowling 1991) and is known as Boltzmann's *Stosszahlansatz*. Boltzmann's derivation would be a central topic in a more advanced course on Kinetic Theory (e.g., Dellar 2015).

### 5.1. *Inhomogeneous Distributions*

We have so far discussed a very simple situation in which the gas was homogeneous, so the velocity pdf $f(\boldsymbol{v})$ described the state of affairs at any point in space and quantities such as $n$, $P$, $T$ were constants in space. This also meant that we could assume that there were no flows (if there was a constant mean flow $\boldsymbol{u}$, we could always go to the frame moving with it). This is obviously not the most general situation: thus, we know from experience that if we open a window from a warm room onto a cold Oxford autumn, it will be colder near the window than far away from it (so $T$ will be a function of space), a draft may develop (mean flow $\boldsymbol{u}$ of air, with some gradients across the room), etc. Clearly such systems will have a particle velocity distribution that is different in different places. Let us therefore generalise our notion of the velocity pdf and introduce *the particle distribution function in the position and velocity space* ("phase space"):

$F(t,\boldsymbol{r},\boldsymbol{v})\mathrm{d}^3\boldsymbol{r}\mathrm{d}^3\boldsymbol{v}$ = average number of particles with velocities in the 3D $\boldsymbol{v}$-space volume $[v_x, v_x+\mathrm{d}v_x]\times[v_y, v_y+\mathrm{d}v_y]\times[v_z, v_z+\mathrm{d}v_z]$ finding themselves in the spatial cube $[x, x+\mathrm{d}x]\times[y, y+\mathrm{d}y]\times[z, z+\mathrm{d}z]$ at time $t$.

I have followed convention in choosing the normalisation

$$\int \mathrm{d}^3\boldsymbol{r}\int \mathrm{d}^3\boldsymbol{v}\, F(t,\boldsymbol{r},\boldsymbol{v}) = N, \tag{5.1}$$

the total number of particles (rather than 1). Clearly, the *0-th velocity moment* of $F$ is the (position- and time-dependent) particle number density:

$$\int \mathrm{d}^3\boldsymbol{v}\, F(t,\boldsymbol{r},\boldsymbol{v}) = n(t,\boldsymbol{r}), \tag{5.2}$$

which integrates to the total particle number:

$$\int \mathrm{d}^3\boldsymbol{r}\, n(t,\boldsymbol{r}) = N \tag{5.3}$$

(the $\boldsymbol{r}$ integrals are always over the system's volume $V$). Note that in a homogeneous system,

$$n(\boldsymbol{r}) = n = \text{const} \quad \text{and} \quad F(\boldsymbol{r},\boldsymbol{v}) = F(\boldsymbol{v}) = nf(\boldsymbol{v}), \tag{5.4}$$

which gets us back to our old familiar homogeneous velocity pdf $f(\boldsymbol{v})$ (which integrates to 1 over the velocity space).

If we know $F(t,\boldsymbol{r},\boldsymbol{v})$, we can calculate other bulk properties of the gas, besides its density (5.2), by taking *moments* of $F$, i.e., integrals over velocity space of various powers of $\boldsymbol{v}$ multiplied by $F$.

Thus, the *first moment*,

$$\int \mathrm{d}^3\boldsymbol{v}\, m\boldsymbol{v}F(t,\boldsymbol{r},\boldsymbol{v}) = mn(t,\boldsymbol{r})\boldsymbol{u}(t,\boldsymbol{r}), \tag{5.5}$$

is the *mean momentum density*, where $\boldsymbol{u}(t,\boldsymbol{r})$ is the mean velocity of the gas flow (without the factor of $m$, this expression, $n\boldsymbol{u}$, is the *mean particle flux*).

A *second moment* gives the *mean energy density*:

$$\int d^3\boldsymbol{v}\,\frac{mv^2}{2}\,F(t,\boldsymbol{r},\boldsymbol{v}) = \int d^3\boldsymbol{w}\,\frac{m|\boldsymbol{u}+\boldsymbol{w}|^2}{2}\,F$$
$$= \frac{mu^2}{2}\underbrace{\int d^3\boldsymbol{w}\,F}_{=n(t,\boldsymbol{r})} + m\boldsymbol{u}\cdot\underbrace{\int d^3\boldsymbol{w}\,\boldsymbol{w}F}_{\substack{=0 \text{ by}\\ \text{definition}\\ \text{of } \boldsymbol{w}}} + \int d^3\boldsymbol{w}\,\frac{mw^2}{2}\,F$$
$$= \underbrace{\frac{mnu^2}{2}}_{\substack{\text{energy density of}\\ \text{mean motions;}\\ \boldsymbol{u}(t,\boldsymbol{r}) \text{ is given}\\ \text{by (5.5)}}} + \underbrace{\left\langle\frac{mw^2}{2}\right\rangle n}_{\substack{\equiv \varepsilon(t,\boldsymbol{r}),\\ \text{internal-energy}\\ \text{density (motions}\\ \text{around the mean)}}}, \tag{5.6}$$

where we have utilised the decomposition of particle velocities into mean and peculiar parts, $\boldsymbol{v} = \boldsymbol{u}(t,\boldsymbol{r}) + \boldsymbol{w}$ (cf. §1.2), where $\boldsymbol{u}$ is defined by (5.5). The total "ordered" energy and the total internal ("disordered") energy are [cf. (1.9)]

$$K = \int d^3\boldsymbol{r}\,\frac{mnu^2}{2} \quad \text{and} \quad U = \int d^3\boldsymbol{r}\,\varepsilon(t,\boldsymbol{r}), \tag{5.7}$$

respectively.

So how do we calculate $F(t,\boldsymbol{r},\boldsymbol{v})$?

## 5.2. *Local Maxwellian Equilibrium*

Recall that we attributed the dependence of $F$ on $\boldsymbol{r}$ and $t$ to certain *macroscopic* inhomogeneities of the system (open windows etc.). It is reasonable, for a wide class of systems, to assume that the spatial ($l$) and temporal ($t$) scales of these inhomogeneities are much greater than $\lambda_{\rm mfp}$ and $\tau_{\rm c}$ in our gas:[19]

$$l \gg \lambda_{\rm mfp}, \quad t \gg \tau_{\rm c}. \tag{5.8}$$

Then we can break up our gas into "fluid elements" of size $\Delta l$ and consider them for a time $\Delta t$ such that

$$l \gg \Delta l \gg \lambda_{\rm mfp}, \quad t \gg \Delta t \gg \tau_{\rm c}. \tag{5.9}$$

Clearly, on these "intermediate" scales, the fluid elements will behave as little homogeneous systems, with locally constant density $n$, moving at some locally constant mean velocity $\boldsymbol{u}$. We can then go to the frame moving with this local velocity $\boldsymbol{u}$ (i.e., following the fluid element) and expect that all our old results derived for a homogeneous static volume of gas will apply—in particular, we should expect the gas making up each fluid element to attain, on the collisional time scale $\tau_{\rm c}$, the *local Maxwellian equilibrium:*

$$\boxed{F_{\rm M}(t,\boldsymbol{r},\boldsymbol{v}) = n(t,\boldsymbol{r})\left[\frac{m}{2\pi k_{\rm B}T(t,\boldsymbol{r})}\right]^{3/2}\exp\left[-\frac{m|\boldsymbol{v}-\boldsymbol{u}(t,\boldsymbol{r})|^2}{2k_{\rm B}T(t,\boldsymbol{r})}\right] = \frac{n}{(\sqrt{\pi}v_{\rm th})^3}\,e^{-w^2/v_{\rm th}^2}}. \tag{5.10}$$

Here $n$ and $v_{\rm th} = \sqrt{2k_{\rm B}T/m}$ are both functions of $t$ and $\boldsymbol{r}$.

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[19] So we are now treating the limit opposite to what we considered when discussing effusion (§3).

Everything is as before, but now locally: e.g., the pressure is [cf. (1.29)]

$$P(t,\boldsymbol{r}) = n(t,\boldsymbol{r})k_{\rm B}T(t,\boldsymbol{r}) = \frac{2}{3}\,\varepsilon(t,\boldsymbol{r}) \tag{5.11}$$

and, therefore, the *local temperature* is, by definition, 2/3 of the mean internal energy per particle:

$$k_{\rm B}T(t,\boldsymbol{r}) = \frac{2}{3}\frac{\varepsilon(t,\boldsymbol{r})}{n(t,\boldsymbol{r})} = \frac{2}{3}\left\langle\frac{mw^2}{2}\right\rangle = \langle m w_x^2\rangle \tag{5.12}$$

[cf. (2.22) and (2.23)].

It is great progress to learn that *only three functions on a 3D space ($\boldsymbol{r}$), viz., $n$, $\boldsymbol{u}$, and $T$, completely describe the particle distribution in the 6D phase space ($\boldsymbol{v}$, $\boldsymbol{r}$).*[20] How then do we determine these three functions?

Thermodynamics gives us a hint as to how they will evolve in time. We know that if we put in contact two systems with different $T$, their temperatures will tend to equalise—so *temperature gradients* between fluid elements must tend to relax—and this should be a collisional process because that is how contact between particles with different energies is made. Same is true about *velocity gradients* (I will prove this thermodynamically in §10.4). But Thermodynamics just tells us that everything must tend from local to *global equilibrium* (no gradients)—not *how fast* that happens or what the intermediate stages in this evolution look like. Kinetic Theory will allow us to describe this *route to equilibrium* quantitatively. We will also see what happens when systems are constantly *driven* out of equilibrium (§§5.6.4–5.6.6).

But before bringing the full power of Kinetic Theory to bear on this problem (in §6), let us first consider what can be said *a priori* about the evolution of $n$, $\boldsymbol{u}$ and $T$.[21]

### 5.3. *Conservation Laws*

Clearly, the evolution of $n$, $\boldsymbol{u}$ and $T$ must be constrained by *conservation laws*. Indeed, if our system is closed and insulated, whatever happens in it must respect the conservation of the total number of particles:

$$\int {\rm d}^3\boldsymbol{r}\, n = N = {\rm const}, \tag{5.13}$$

of the total momentum:

$$\int {\rm d}^3\boldsymbol{r}\, mn\boldsymbol{u} = 0 = {\rm const} \tag{5.14}$$

(0 because we can work in the frame moving with the centre of mass of the system), and of the total energy:

$$\int {\rm d}^3\boldsymbol{r}\left(\frac{mnu^2}{2} + \underbrace{\varepsilon}_{=\frac{3}{2}nk_{\rm B}T}\right) = K + U = {\rm const}. \tag{5.15}$$

[20] NB: in §6.2, we will learn that, in fact, fluxes of momentum and energy—and, therefore, transport phenomena—arise from small deviations of $F$ from the local Maxwellian. Thus, the local Maxwellian is not the whole story and even to determine the three functions that specify this local Maxwellian, we will need to calculate how the particle distribution differs from it.

[21] In the words of J. B. Taylor, one always ought to know the answer before doing the calculation, "we don't do the bloody calculation because we don't know the answer, we do it because we have a conscience!"

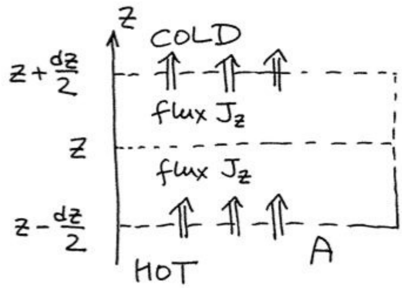


FIGURE 11. Heat flux, see (5.17).

Without knowing any Kinetic Theory, can we establish from these constraints the general form of the evolution equations for $n$, $\boldsymbol{u}$ and $T$? Yes, we can!

5.3.1. *Temperature*

For simplicity, let us first consider a situation in which nothing moves on average ($\boldsymbol{u} = 0$) and $n = \text{const}$ globally. Then all energy in the system is internal energy,

$$\varepsilon = nc_1 T(t, \boldsymbol{r}) \tag{5.16}$$

and only temperature is inhomogeneous. Here $c_1$ is the heat capacity per particle: for a monatomic ideal gas, $c_1 = 3k_\text{B}/2$, but I will use $c_1$ in what follows to mark the results that are valid also for gases or other substances with different values of $c_1$—because these results are reliant on conservation of energy and little else.[22]

To simplify even further, consider a 1D problem, where $T = T(t, z)$ varies in one direction only. Internal energy (heat) will flow from hot to cold regions (as we know from Thermodynamics), so there will be a *heat flux*:

$J_z(z) =$ internal energy flowing along $z$ per unit time through unit area perpendicular to the $z$ axis.

Then the rate of change of internal energy in a small volume $A \times [z - \text{d}z/2, z + \text{d}z/2]$ ($A$ is area; see Fig. 11) is[23]

$$\frac{\partial}{\partial t} \underbrace{nc_1 T \cdot A\text{d}z}_{\substack{\text{energy in the}\\ \text{volume } A\text{d}z}} = \underbrace{J_z\left(z - \frac{\text{d}z}{2}\right) \cdot A}_{\substack{\text{energy}\\ \text{flowing in}}} - \underbrace{J_z\left(z + \frac{\text{d}z}{2}\right) \cdot A}_{\substack{\text{energy}\\ \text{flowing out}}}. \tag{5.17}$$

[22]Furthermore, $n = \text{const}$ is a very good approximation for liquids and solids, but, in fact, quite a bad one for a gas, even if all its motions are subsonic. There is a subtlety here, related to the gas wanting to be in pressure balance—this is discussed at the end of §6.4.2 [around (6.25)], but I will ignore it for now, for the sake of simplicity and to minimise the amount of algebra in this initial derivation. Obviously, everything can be derived without these simplifications: the full correct temperature equation is derived on general energy-conservation grounds in Exercise 5.3 [see (5.37)] and systematically as part of the kinetic theory of transport in §6.4.3 [see (6.39)].

[23]Note that incompressibility ($n = \text{const}$) is useful here as it allows us not to worry about the net flux of matter into (or out of) our volume. In the more general, compressible, case, this contribution to the rate of change of internal energy turns up in the form of the $\boldsymbol{\nabla} \cdot \boldsymbol{u}$ term in (5.37).

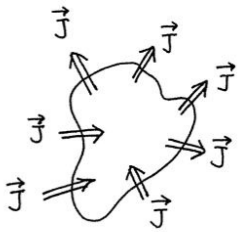


FIGURE 12. Heat flows into or out of an arbitrary volume.

This instantly gives

$$nc_1 \frac{\partial T}{\partial t} = -\frac{J_z\left(z + \frac{\mathrm{d}z}{2}\right) - J_z\left(z - \frac{\mathrm{d}z}{2}\right)}{\mathrm{d}z} = -\frac{\partial J_z}{\partial z}, \quad \text{as } \mathrm{d}z \to 0. \tag{5.18}$$

It is very easy to generalise this to a 3D situation. The rate of change of internal energy in an arbitrary volume $V$ is

$$\frac{\partial}{\partial t} \underbrace{\int_V \mathrm{d}^3\boldsymbol{r}\, nc_1 T}_{\substack{\text{energy in}\\ \text{volume } V}} = -\underbrace{\int_{\partial V} \mathrm{d}\boldsymbol{A}\cdot\boldsymbol{J}}_{\substack{\text{flux through}\\ \text{the boundary}\\ \text{of the volume}}} = -\int_V \mathrm{d}^3\boldsymbol{r}\, \boldsymbol{\nabla}\cdot\boldsymbol{J}, \tag{5.19}$$

where I have used Gauss's theorem. The heat flux is now a vector, $\boldsymbol{J}$, pointing in the direction in which the heat flows (Fig. 12). Since $V$ can be chosen completely arbitrarily, the integral relation (5.19) becomes a differential one:

$$\boxed{nc_1 \frac{\partial T}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{J}}\ . \tag{5.20}$$

This is of course just a local statement of energy conservation.

Thus, *if we can calculate the heat flux, $\boldsymbol{J}$, we can determine the evolution of $T$.*

---

**Exercise 5.1. Electromagnetism: Charge and Energy Conservation.** (a) Prove (from Maxwell's equations) that the Coulomb charge density $\rho$ and the current density $\boldsymbol{j}$ (which is the flux of charge) are related by

$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{j}. \tag{5.21}$$

Show that this also follows from the conservation of charge.

(b) The energy density of the electromagnetic field is (in Gauss units)

$$\varepsilon = \frac{E^2 + B^2}{8\pi}. \tag{5.22}$$

What is the flux of this energy (in terms of $\boldsymbol{E}$ and $\boldsymbol{B}$)? Is the electromagnetic energy conserved? (if not, where does it go?) This is an opportunity to check whether you understand E&M.

**Exercise 5.2. Continuity Equation.** Now consider a gas with some mean flow velocity $\boldsymbol{u}(t, \boldsymbol{r})$ and density $n(t, \boldsymbol{r})$, both varying in (3D) space and time. What is the flux of particles through a surface within such a system? Use the requirement of particle conservation to derive *the continuity equation*

$$\frac{\partial n}{\partial t} = -\boldsymbol{\nabla}\cdot(n\boldsymbol{u}). \tag{5.23}$$

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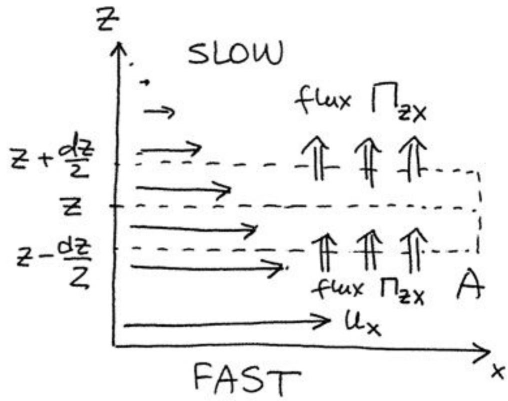


FIGURE 13. Momentum flux, see (5.26).

Note that (5.23) can be rewritten as

$$\left(\frac{\partial}{\partial t} + \boldsymbol{u}\cdot\boldsymbol{\nabla}\right) n = -n\boldsymbol{\nabla}\cdot\boldsymbol{u}. \tag{5.24}$$

The left-hand side is the so-called *convective time derivative* of $n$—the rate of change of density in a fluid element moving with velocity $\boldsymbol{u}$ (think about why that is; we will use similar logic in §6.3). The above equation then means that a negative divergence of the gas flow, $\boldsymbol{\nabla}\cdot\boldsymbol{u} < 0$, implies local compression, whereas positive divergence, $\boldsymbol{\nabla}\cdot\boldsymbol{u} > 0$, implies local rarefaction.

In fact, you know all this from your first-year maths.

---

5.3.2. *Velocity*

We can handle momentum conservation in a similar fashion. Let us again assume $n = \text{const}$, but allow a $z$-dependent flow velocity in the $x$ direction (this is called a *shear flow*):

$$\boldsymbol{u} = u_x(t, z)\hat{\boldsymbol{x}}. \tag{5.25}$$

In this system, momentum will flow from fast- to slow-moving layers of the gas (because, as we will learn below, they experience friction against each other, due to particle collisions). Let us define the *momentum flux*:

$\mathit{\Pi}_{zx}(z) =$ momentum in the $x$ direction flowing along $z$ per unit time through unit area perpendicular to the $z$ axis.

Then, analogously to (5.17) (see Fig. 13),

$$\frac{\partial}{\partial t}\underbrace{mnu_x\cdot A\mathrm{d}z}_{\substack{\text{momentum in}\\ \text{the volume}\\ A\mathrm{d}z}} = \underbrace{\mathit{\Pi}_{zx}\left(z-\frac{\mathrm{d}z}{2}\right)\cdot A}_{\substack{\text{momentum}\\ \text{flowing in}}} - \underbrace{\mathit{\Pi}_{zx}\left(z+\frac{\mathrm{d}z}{2}\right)\cdot A}_{\substack{\text{momentum}\\ \text{flowing out}}}, \tag{5.26}$$

whence

$$\boxed{mn\frac{\partial u_x}{\partial t} = -\frac{\partial \mathit{\Pi}_{zx}}{\partial z}}\,. \tag{5.27}$$

Thus, *in order to determine the evolution of velocity, we must calculate the momentum flux.*

---

Let us generalise this calculation. Let $n(t, \boldsymbol{r})$ and $\boldsymbol{u}(t, \boldsymbol{r})$ both be functions of space and time.

Considering an arbitrary volume $V$ of the gas, we can write the rate of change of momentum in it as

$$\frac{\partial}{\partial t}\int_V \mathrm{d}^3\boldsymbol{r}\, mn\boldsymbol{u} = -\int_{\partial V} \mathrm{d}\boldsymbol{S}\cdot\boldsymbol{\mathit{\Pi}}, \tag{5.28}$$

or, in tensor notation,

$$\frac{\partial}{\partial t}\int_V \mathrm{d}^3\boldsymbol{r}\, mnu_j = -\int_{\partial V} \mathrm{d}S_i \mathit{\Pi}_{ij}. \tag{5.29}$$

The momentum flux is now a tensor (also known as the *stress tensor*): $\mathit{\Pi}_{ij}$ is the flux of the $j$-th component of momentum in the $i$ direction (in the case of the shear flow, this tensor only had one non-zero component, $\mathit{\Pi}_{zx}$). Application of Gauss's Theorem gives us

$$\frac{\partial}{\partial t} mnu_j = -\partial_i \mathit{\Pi}_{ij}. \tag{5.30}$$

The momentum flux consists of three parts:

—one (*"convective"*) due to the fact that the boundary of a fluid element containing the same particles itself moves with velocity $\boldsymbol{u}$: the flux of the $j$-th component of the momentum, $mnu_j$, due to this effect is $mnu_j\boldsymbol{u}$ and so

$$\mathit{\Pi}_{ij}^{(\mathrm{convective})} = mnu_iu_j, \tag{5.31}$$

i.e., momentum "carries itself" (just like it carries particle density: recall the flux of particles being $n\boldsymbol{u}$ in (5.23));

—one due to the fact that there is pressure in the system and pressure is also momentum flux, viz., the flux of each component of the momentum in the direction of that component (recall §1.4: particles with velocity component $v_z$ transfer momentum in the $z$ direction to the wall perpendicular to $z$—in our current calculation, this pressure acts on the boundary of our chosen volume $V$); thus, the pressure part of the momentum flux is diagonal:

$$\mathit{\Pi}_{ij}^{(\mathrm{pressure})} = P\delta_{ij}; \tag{5.32}$$

—and, finally, one due to friction between layers of gas moving at different velocities; as we have seen in §5.3.2, this part of the momentum-flux tensor, $\mathit{\Pi}_{ij}^{(\mathrm{viscous})}$, will contain off-diagonal elements, but we have not yet worked out how to calculate them.

Substituting these three contributions, viz.,

$$\mathit{\Pi}_{ij} = mnu_iu_j + P\delta_{ij} + \mathit{\Pi}_{ij}^{(\mathrm{viscous})}, \tag{5.33}$$

into (5.30), we get

$$\frac{\partial}{\partial t} mn\boldsymbol{u} = -\boldsymbol{\nabla}\cdot(mn\boldsymbol{u}\boldsymbol{u}) - \boldsymbol{\nabla}P - \boldsymbol{\nabla}\cdot\boldsymbol{\mathit{\Pi}}^{(\mathrm{viscous})}, \tag{5.34}$$

or, after using (5.23) to express $\partial n/\partial t$,

$$mn\left(\frac{\partial\boldsymbol{u}}{\partial t} + \boldsymbol{u}\cdot\boldsymbol{\nabla}\boldsymbol{u}\right) = -\boldsymbol{\nabla}P - \boldsymbol{\nabla}\cdot\boldsymbol{\mathit{\Pi}}^{(\mathrm{viscous})}. \tag{5.35}$$

This is the desired generalisation of (5.27)—the evolution equation for the mean flow velocity $\boldsymbol{u}(t,\boldsymbol{r})$. This equation says that fluid elements move around at their own velocity (the convective time derivative in the left-hand side) and are subject to forces arising from pressure gradients and friction (the right-hand side); if there are any other forces in the system, e.g., gravity, those have to be added to the right-hand side of (5.35). Obviously, we still need to calculate $\boldsymbol{\mathit{\Pi}}^{(\mathrm{viscous})}$ in order for this equation to be useful in actual calculations.

In §6.4.2, (5.35) will be derived from kinetic theory.

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**Exercise 5.3. Energy Flows.** Generalise (5.20) to the case of non-zero flow velocity $\boldsymbol{u}(t,\boldsymbol{r}) \neq 0$ and non-constant $n(t,\boldsymbol{r})$. Consider the total energy density of the fluid,

$$\frac{mnu^2}{2} + \frac{3}{2}nk_{\mathrm{B}}T, \tag{5.36}$$

and calculate the rate of change of the total energy inside a volume $V$ due to energy being carried by the flow $\boldsymbol{u}$ through the boundary $\partial V$, work done by pressure and by viscous stresses on that boundary, and heat flowing through the boundary. If you use (5.23) and (5.35) to work out the time derivatives of $n$ and $\boldsymbol{u}$, in the end you should be left with the following evolution equation for $T$:

$$\frac{3}{2}nk_{\mathrm{B}}\left(\frac{\partial T}{\partial t}+\boldsymbol{u}\cdot\boldsymbol{\nabla}T\right)=-\boldsymbol{\nabla}\cdot\boldsymbol{J}-nk_{\mathrm{B}}T\boldsymbol{\nabla}\cdot\boldsymbol{u}-\mathit{\Pi}_{ij}^{(\mathrm{viscous})}\partial_i u_j. \tag{5.37}$$

Interpret all the terms and identify the conditions under which the gas behaves *adiabatically*, i.e., satisfies

$$\left(\frac{\partial}{\partial t}+\boldsymbol{u}\cdot\boldsymbol{\nabla}\right)\frac{P}{n^{5/3}}=0. \tag{5.38}$$

In §6.4.3, (5.37) will be derived from kinetic theory.

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### 5.4. *Thermal Conductivity and Viscosity*

So, we have evolution equations for temperature and velocity, (5.18) and (5.27) (sticking with the 1D case), which are local expressions of energy and momentum conservation laws containing the as yet unknown fluxes $J_z$ and $\mathit{\Pi}_{zx}$. In (relatively) short order, we will learn how to calculate these fluxes from kinetic theory (i.e., from particle distributions)—we can be optimistic about being able to do this in view of our experience of calculating fluxes in the effusion problem (§3; effusion was transport on scales $\ll \lambda_{\mathrm{mfp}}$, what we need now is transport on scales $\gg \lambda_{\mathrm{mfp}}$). However, first let us ask *a priori* what the answer should look like.

From thermodynamics (heat flows from hot to cold), we expect that

- $J_z \neq 0$ only if $\partial T/\partial z \neq 0$,
- $J_z$ has the opposite sign to $\partial T/\partial z$.

Similarly, $\mathit{\Pi}_{zx} \neq 0$ only if $\partial u_x/\partial z \neq 0$ and also has the opposite sign. It is then a plausible conjecture that *fluxes will just be proportional to (minus) gradients*—indeed this is more or less inevitable if the gradients are in some sense (to be made precise in §5.6.3) not very large, because we can simply Taylor-expand the fluxes, which are clearly functions of the gradients, around zero values of these gradients:

$$J_z\left(\frac{\partial T}{\partial z}\right)=\underbrace{J_z(0)}_{=0}+J_z'(0)\frac{\partial T}{\partial z}+\dots\approx-\varkappa\frac{\partial T}{\partial z}, \tag{5.39}$$

$$\mathit{\Pi}_{zx}\left(\frac{\partial u_x}{\partial z}\right)=\underbrace{\mathit{\Pi}_{zx}(0)}_{=0}+\mathit{\Pi}_{zx}'(0)\frac{\partial u_x}{\partial z}+\dots\approx-\eta\frac{\partial u_x}{\partial z}, \tag{5.40}$$

where we have introduced two (we expect, positive) *transport coefficients:*

- *the thermal conductivity* $\varkappa$,
- *the dynamical viscosity* $\eta$.

These quantities are introduced in the same spirit as various susceptibilities and other response functions in Thermodynamics: except here, we are relating non-equilibrium quantities: macroscopic gradients and fluxes.

---

In 3D, the heat flux is (obviously)

$$\boldsymbol{J}=-\varkappa\boldsymbol{\nabla}T, \tag{5.41}$$

whereas the viscous part of the stress tensor [appearing in (5.35)] is

$$\boldsymbol{\mathit{\Pi}}^{(\mathrm{viscous})}=-\eta\left[\boldsymbol{\nabla}\boldsymbol{u}+(\boldsymbol{\nabla}\boldsymbol{u})^T-\frac{2}{3}\mathsf{I}\,\boldsymbol{\nabla}\cdot\boldsymbol{u}\right], \tag{5.42}$$

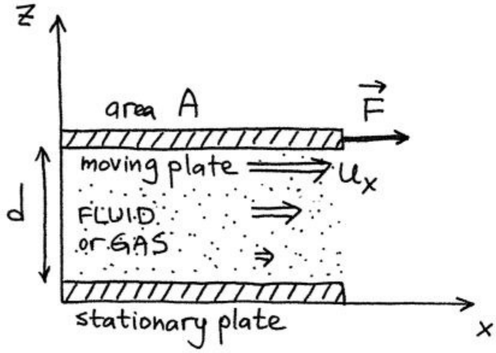


FIGURE 14. (Gedanken) experiment to define and determine viscosity; see (5.43).

where $\mathbf{I}$ is a unit matrix. The latter expression is not immediately obvious—I will derive it (extracurricularly) in §6.8 [see (6.74)].

---

The proportionalities between fluxes and gradients expressed by (5.39) and (5.40) do indeed turn out to hold, experimentally, for a good range of physical parameters ($n$, $P$, $T$) and for very many substances (gases, fluids, or, in the case of (5.39), even solids). The coefficients $\varkappa$ and $\eta$ can be experimentally measured and tabulated even if we know nothing of kinetics or microphysics. It is thus that physics—and certainly engineering!—often manage to get to workable models without necessarily achieving complete understanding right away.

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For example, viscosity can be introduced and measured as follows. Set up an experiment with two horizontal plates of area $A$ at a vertical distance $d$ from each other and a fluid (or gas) between them, the lower plate stationary, the upper one being moved at a horizontal velocity $u_x$ (Fig. 14). If one measures the force $F$ that one needs to apply to the upper plate in order to maintain a constant $u_x$, one discovers that, for small enough $d$,

$$\boxed{\frac{F}{A} = \eta\,\frac{u_x}{d} \approx \eta\,\frac{\partial u_x}{\partial z}}\,, \tag{5.43}$$

where $\eta$ is a dimensional coefficient independent of $u_x$, $d$, or $A$, and approximately constant in a reasonable range of physical conditions for any particular type of inter-plate substance used. By definition, $\eta$ is the *dynamical viscosity* of that substance. The left-hand side of (5.43) is force (=momentum per time) per area, which is the momentum flux downward from the upper plate to the lower, $F/A = -\Pi_{zx}$, and so (5.40) is recovered.

The physics of momentum transport here is straightforward: the upper plate moves, the molecules of gas immediately adjacent to that plate collide with it, receive some momentum, eventually make their way some distance downward, collide with molecules in a lower layer of gas, pass some momentum to them, those in turn collide with molecules further down, etc. (in the case of a fluid, we would talk about the layer immediately adjacent to the moving plate sticking to it and passing momentum via friction to the next layer lower down, etc.).

---

Note that the relationships (5.39) and (5.40) are valid much more generally than will be the upcoming expressions for $\varkappa$ and $\eta$ that we will derive for ideal gas. Thus, we can talk about the viscosity of water or thermal conductivity of a metal, although neither obviously can be viewed as a collection of non-interacting billiard-ball particles on any level of simplification.

5.5. *Transport Equations*

If we now substitute (5.39) and (5.40) into (5.18) and (5.27), we obtain closed equations for $T$ and $u_x$:

$$nc_1 \frac{\partial T}{\partial t} = \varkappa \frac{\partial^2 T}{\partial z^2}, \tag{5.44}$$

$$mn \frac{\partial u_x}{\partial t} = \eta \frac{\partial^2 u_x}{\partial z^2}. \tag{5.45}$$

These are the *transport equations* that we were after.

Note that in pulling $\varkappa$ and $\eta$ out of the $z$ derivative, we assumed them to be independent of $z$: this is fine even though they do depend on $T$ (which depends on $z$) as long as the temperature gradients and, therefore, the temperature differences are not large on the scales that we are considering and so $\varkappa$ and $\eta$ can be approximated by constant values taken at some reference temperature.

---

Let us make this quantitative. Let $\varkappa = \varkappa(T)$ and assume that $T = T_0 + \delta T$, where $T_0 = \text{const}$ and all the temperature variation is contained in the small perturbation $\delta T(t, z) \ll T_0$. This is indeed a commonplace situation: temperature variations in our everyday environment rarely exceed $\sim 10\%$ of the absolute temperature $T \sim 300$ K. Then

$$\varkappa(T) \approx \varkappa(T_0) + \varkappa'(T_0)\delta T \tag{5.46}$$

and so, from (5.18) and (5.39),

$$nc_1 \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\varkappa(T)\frac{\partial T}{\partial z} \approx \varkappa(T_0)\frac{\partial^2 \delta T}{\partial z^2} + \varkappa'(T_0)\frac{\partial}{\partial z}\delta T \frac{\partial \delta T}{\partial z}, \tag{5.47}$$

but the second term is quadratic in the small quantity $\delta T$ and so can be neglected, giving us back (5.44) (after $\delta T$ in the diffusion term is replaced by $T$, which is legitimate because the constant part $T_0$ vanishes under gradients).

If you would like to learn how to analyse systems where $\delta T$ is not small (and, along the way, to be introduced to the beautiful world of scaling and self-similar solutions) read Barenblatt (2003, 1996) (the 2003 book is easier as a first read).

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5.6. *Relaxation to Global Equilibrium*

Let us now form some idea of the nature of the solutions to the transport equations (5.44) and (5.45): what do they tell us about the time evolution of temperature and velocity? Recall that the motivation of this entire line of inquiry was our expectation that the gas would get to *local* Maxwellian equilibrium (§5.2) over a few collision times and then slowly evolve towards a *global* Maxwellian equilibrium, in which all spatial gradients in $n$, $\boldsymbol{u}$ or $T$ would be erased. We are about to see that this is exactly the behaviour that (5.44) and (5.45) describe.

It is apposite to notice here that *these equations have the same mathematical structure*: they are both *diffusion equations* (why that is, physically, will be discussed in §5.7). Let us write them explicitly in this form:

$$\frac{\partial T}{\partial t} = D_T \frac{\partial^2 T}{\partial z^2}, \tag{5.48}$$

$$\frac{\partial u_x}{\partial t} = \nu \frac{\partial^2 u_x}{\partial z^2}. \tag{5.49}$$

The temperature (equivalently, energy) diffusion coefficient is the *thermal diffusivity*, related to the thermal conductivity in a simple fashion:

$$D_T = \frac{\varkappa}{nc_1}. \tag{5.50}$$

Similarly, the velocity (or momentum) diffusion coefficient is the *kinematic viscosity*, related to the dynamical viscosity as

$$\nu = \frac{\eta}{mn}. \tag{5.51}$$

Since the Laplacian ($\nabla^2$, or $\partial^2/\partial z^2$ in 1D) is a negative definite operator, (5.48) and (5.49) describe gradual relaxation with time of temperature and velocity gradients, provided $D_T > 0$ and $\nu > 0$—relaxation to a global, homogeneous Maxwellian equilibrium.

### 5.6.1. *Initial-Value Problem*

The simplest way to see this and to estimate the time scales on which this relaxation will occur is to consider an initial-value problem for, e.g., (5.48) with some boundary conditions that allow decomposition of the initial condition and the solution into a Fourier series (or, more generally, a Fourier integral). If the initial temperature distribution is

$$T(t=0,z) = \sum_k \hat{T}_0(k)e^{ikz}, \tag{5.52}$$

then the solution of (5.48),

$$T(t,z) = \sum_k \hat{T}(t,k)e^{ikz}, \tag{5.53}$$

satisfies

$$\frac{\partial \hat{T}}{\partial t} = -D_T k^2 \hat{T} \quad \Rightarrow \quad \hat{T}(t,k) = \hat{T}_0(k)e^{-D_T k^2 t}. \tag{5.54}$$

Thus, *spatial variations ($k \neq 0$) of temperature relax exponentially fast in time on the diffusion time scale:*

$$\hat{T}(t,k) \propto e^{-t/\tau_{\rm diff}}, \quad \tau_{\rm diff} = \frac{1}{D_T k^2} \sim \frac{l^2}{D_T}, \tag{5.55}$$

where $l \sim k^{-1}$ is the typical spatial scale of the variation and $\tau_{\rm diff}$ is, therefore, its typical time scale.

Using (5.53) and (5.54), one can reconstruct the full solution of (5.48) given the initial perturbation (5.52):

$$T(t,z) = \sum_k \hat{T}_0(k)\, e^{ikz - D_T k^2 t}. \tag{5.56}$$

Here $\hat{T}_0(k)$ can be expressed as the inverse Fourier transform of $T(t=0,z)$, from (5.52):

$$\hat{T}_0(k) = \frac{1}{L}\int {\rm d}z'\, T(t=0,z')\, e^{-ikz'}, \tag{5.57}$$

where $L$ is the length of the domain in $z$. Substituting this into (5.56) and replacing the sum over $k$ with an integral (which we can do if we notice that, in a periodic domain of size $L$, the "mesh" size in $k$ is $2\pi/L$),

$$\sum_k = \frac{L}{2\pi}\int {\rm d}k, \tag{5.58}$$

we get

$$T(t,z) = \frac{1}{2\pi}\int {\rm d}z'\, T(t=0,z') \int {\rm d}k\, e^{ik(z-z') - D_T k^2 t}. \tag{5.59}$$

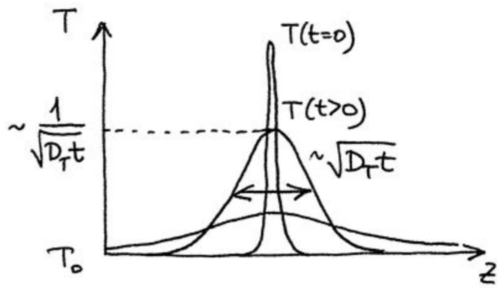



FIGURE 15. Diffusive spreading of an initial hot spike; see (5.60).

After the $k$ integral is done by completing the square in the exponential, the result is

$$\boxed{T(t,z) = \int \mathrm{d}z'\, T(t=0,z')\, \frac{1}{\sqrt{4\pi D_T t}} \exp\left[-\frac{(z-z')^2}{4D_T t}\right]}. \tag{5.60}$$

This formula is an example of a *Green's-function solution* of a partial differential equation. It describes the initial perturbation spreading as $z - z' \sim \sqrt{D_T t}$, a behaviour known as the *random walk*, and related to the Central Limit Theorem in §5.7.2. The easiest way to see this is to imagine that the initial perturbation is a sharp spike at the origin, $T(t=0,z) = \delta(z)$. After time $t$, this spike turns into a Gaussian-shaped profile with rms width $= \sqrt{2D_T t}$ (Fig. 15).

The velocity diffusion governed by (5.49) is entirely analogous to the temperature diffusion.

Recall that in arguing for a local Maxwellian, we required the assumption that *the transport scales, $l$ and $\tau_{\rm diff}$, were much greater than the spatial and time scales of particle collisions, $\lambda_{\rm mfp}$ and $\tau_{\rm c}$* [see (5.8)]. Are they? Yes, but to show this (and to be able to solve practical problems), we still have to derive explicit expressions for $D_T$ and $\nu$.

In what follows, we will do this not once but four times, in four different ways (which highlight different aspects of the problem):

• a dimensional guess, scoundrel's last (or, in our case, first) recourse (§5.6.2),

• an estimate based on modelling collisions as particle diffusion, a physically important insight (§5.7),

• a "pseudo-kinetic" derivation, dodgy but nice and simple (§6.1),

• a "real" kinetic derivation, more involved, but also more systematic, mathematically appealing, and showing how more complicated problems are solved (the rest of §6).

### 5.6.2. *Dimensional Estimate of Transport Coefficients*

As often happens, the quickest way to get the answer (or an answer) is a dimensional guess. The dimensionality of diffusion coefficients is

$$[D_T] = [\nu] = \frac{\text{length}^2}{\text{time}}. \tag{5.61}$$

Clearly, transport of energy and momentum from one part of the system to another is due to particles colliding. Therefore, both the energy- and momentum-diffusion coefficients must depend on some quantities characterising particle collisions. We need a length and a time: well, obviously, the mean free path $\lambda_{\rm mfp}$ and the collision time $\tau_{\rm c}$. Then [using (4.5)]

$$\boxed{D_T \sim \nu \sim \frac{\lambda_{\rm mfp}^2}{\tau_{\rm c}} \sim v_{\rm th}^2\tau_{\rm c} \sim v_{\rm th}\lambda_{\rm mfp}}\,. \tag{5.62}$$

This is indeed true (as properly proved in §6), although of course we cannot determine numerical prefactors from dimensional analysis.

5.6.3. *Separation of Scales*

Armed with the estimate (5.62), we can now ascertain that there indeed is a separation of scales between collisional relaxation to local equilibrium and diffusive relaxation to the global one: the diffusion time (5.55) becomes

$$\tau_{\rm diff} \sim \left(\frac{l}{\lambda_{\rm mfp}}\right)^2 \tau_{\rm c} \gg \tau_{\rm c} \quad \text{if} \quad l \gg \lambda_{\rm mfp}. \tag{5.63}$$

Thus, spatial-scale separation implies time-scale separation, i.e., if we set up some macroscopic ($l \gg \lambda_{\rm mfp}$) temperature gradients or shear flows in the system, they will relax slowly compared to the collision time, with the system evolving through a sequence of local Maxwellian equilibria (5.10) as $T$ or $\boldsymbol{u}$ gradually become uniform.

5.6.4. *Sources, Sinks and Boundaries*

I have so far only discussed the situation where some *initial* non-equilibrium state relaxes freely towards global equilibrium. In the real world, there often are external circumstances that mathematically amount to *sources* or *sinks* in the transport equations and keep the system out of equilibrium even as it ever strives towards it. In such systems, the transport equations can have *steady-state* (time-independent; §5.6.5) or *stationary time-dependent* (periodic; §5.6.6) solutions.

Thus, in the heat diffusion equation (5.44), there can be *heating* and *cooling* terms:

$$nc_1\frac{\partial T}{\partial t} = \varkappa\frac{\partial^2 T}{\partial z^2} + H - C. \tag{5.64}$$

Here the *heating rate* $H$ represents some form of distributed heating, e.g., viscous [the last term in (5.37); see also §6.4.3] or Ohmic (if current can flow through the medium); the *cooling rate* $C$ can, e.g., be due to radiative cooling (usually in very hot gases/plasmas).

Similarly, the momentum equation (5.45) can include external *forces:*

$$mn\frac{\partial u_x}{\partial t} = \eta\frac{\partial^2 u_x}{\partial z^2} + f_x, \tag{5.65}$$

where $f_x$ is the "body force," or force density, in the $x$ direction. Common examples of body forces [for all of which, however, one requires the more general, 3D version of the momentum equation; see (5.35)] are the pressure gradient, gravity, Coriolis and centrifugal forces in rotating systems, Lorentz force in conducting media, buoyancy force in stratified media, etc.

Sources or sinks of heat and momentum can also take the form of *boundary conditions*, e.g.,

—a surface kept at some fixed temperature,

—a given heat flux constantly pumped through a surface (perhaps via the latter being in contact with a heat source generating heat at a given rate),

—a rate of cooling at a surface specified in terms of its temperature (e.g., Newton's law of cooling: cooling rate proportional to the temperature difference between the surface

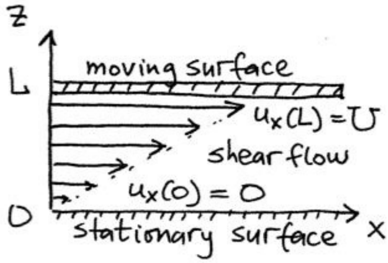
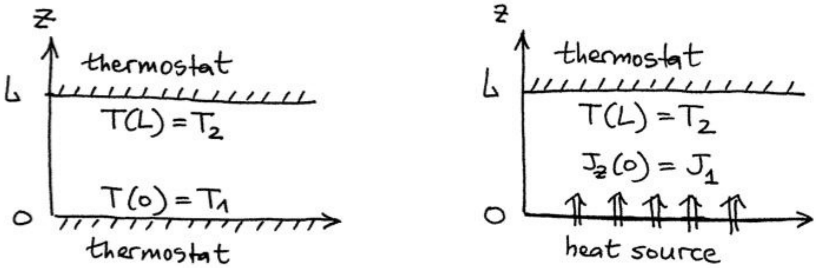



FIGURE 16. Linear shear flow (5.67).




(a) (b)

FIGURE 17. Boundary conditions for the heat diffusion equation: (a) two thermostatted surfaces, (b) a thermostatted surface and a heat source.

of a body and the environment),
—a surface moving at a given velocity, etc.

5.6.5. *Steady-State Solutions*

Steady-state solutions arise when sources, sinks and/or boundary conditions are constant in time and so cause time-independent temperature or velocity profiles to emerge.

For example, the *force balance*

$$\eta\,\frac{\partial^2 u_x}{\partial z^2} + f_x = 0 \tag{5.66}$$

will imply some profile $u_x(z)$, given the spatial dependence of the force $f_x(z)$ and some boundary conditions on $u_x$ (since the diffusion equation is second-order in $z$, two of those are needed). The simplest case is $f_x = 0$, $u_x(0) = 0$, $u_x(L) = U$, which instantly implies, for $z \in [0, L]$

$$u_x(z) = U\,\frac{z}{L}, \tag{5.67}$$

the solution known as *linear shear flow* (Fig. 16).

Similarly, looking for steady-state solutions of (5.44) subject to both ends of the domain being kept at fixed temperatures, $T(0) = T_1$ and $T(L) = T_2$ (Fig. 17a), we find

$$\frac{\partial^2 T}{\partial z^2} = 0 \quad \Rightarrow \quad T(z) = T_1 + (T_2 - T_1)\frac{z}{L}. \tag{5.68}$$

Note that the simple linear profiles (5.67) and (5.68) are entirely independent of the transport coefficients $\varkappa$ and $\eta$.

A slightly more sophisticated example is a set up where, say, the bottom surface of the system is heated at some known fixed rate, i.e., the heat flux through the $z = 0$ boundary is specified, $J_z(0) = J_1$, while the top surface is in contact with a fixed-temperature thermostat, $T(L) = T_2$ (Fig. 17b). Then (5.44) or, indeed, already (5.18) gives, in steady state,

$$\frac{\partial J_z}{\partial z} = 0 \quad \Rightarrow \quad J_z = \text{const} = J_1. \tag{5.69}$$

Since $J_z = -\varkappa \partial T/\partial z$ [see (5.39)],

$$T(z) = \frac{J_1}{\varkappa}(L - z) + T_2, \tag{5.70}$$

a profile that *does* depend on $\varkappa$. From this we learn what the temperature at the bottom boundary is, viz., $T(0) = J_1 L/\varkappa + T_2$, and, therefore, the overall temperature contrast that can be maintained by injection of a given power $J_1$, viz., $\Delta T = J_1 L/\varkappa$.

---

**Exercise 5.4.** Work out the steady-state temperature profile $T(r)$ that will be maintained at the radii $r \in [r_1, r_2]$ in an axisymmetric system where $T(r_1) = T_1$ and $T(r_2) = T_2$.

---

Steady-state profiles of the kind described above, even though they are solutions of the transport equations, are not necessarily *stable* solutions. Time-dependent motions can develop as a result of small perturbations of the steady state (e.g., for convection, given large enough temperature contrasts, the so-called Rayleigh-Bénard problem; see, e.g., Chandrasekhar 2003). Indeed, it is very common for Nature to find such ways of relaxing gradients via instabilities and resulting motions (*turbulence*) when the gradients (deviations from global equilibrium) are strong and collisional/diffusive transport is relatively slow—Nature tends to be impatient with out-of-equilibrium set-ups.

Just how impatient can be estimated very crudely in the following way. One might think of mean fluid motions that develop in a system as carrying heat and momentum in a way somewhat similar to what random-walking particles do (§5.7.2), but now moving parcels of fluid travel at the typical flow velocity $u$ and "collide" after some distance $l$ representing the typical scale of the motions. This gives rise to "turbulent diffusion" with diffusivity $D_{\rm turb} \sim ul$,[24] analogous to $D_T \sim \nu \sim v_{\rm th}\lambda_{\rm mfp}$. Which of these is larger determines which controls transport. Their ratio,

$$\text{Re} = \frac{D_{\rm turb}}{\nu} \sim \frac{u}{v_{\rm th}} \frac{l}{\lambda_{\rm mfp}}, \tag{5.71}$$

known as the *Reynolds number*, is a product of, typically, a small number $(u/v_{\rm th})$ and a large number $(l/\lambda_{\rm mfp})$. The latter usually wins, except in very small systems or when flows are really very slow. In turbulent systems (Re $\gg 1$), the heat and momentum transport is "anomalous", meaning much faster than collisional.

---

### 5.6.6. *Time-Periodic Solutions*

If we now consider a situation in which the boundary condition is time-dependent in some periodic way, e.g., the surface of the system is subject to some seasonal temperature changes, then the solution that will emerge will be time-periodic. Physically, this describes a system whose state is a result of the external conditions constantly driving it out of equilibrium and the heat diffusion constantly pushing it back to equilibrium.

The treatment of such cases is analogous to what we did with the relaxation of an initial inhomogeneity in §5.6.1, but now the Fourier transform is in time rather than in space. So, consider a semi-infinite domain, $z \in [0, \infty)$, with the boundary condition

$$T(t, z = 0) = \sum_\omega \hat{T}_0(\omega) e^{-i\omega t} \tag{5.72}$$

(say a building with the outer wall at $z = 0$ exposed to the elements, with $\omega$'s being the frequencies of daily, annual, centennial etc. temperature variations). Then the solution

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[24]Or $D_{\rm turb} \sim u^2 \tau_{\rm turb} \sim l^2/\tau_{\rm turb}$, where $\tau_{\rm turb} \sim l/u$ is the "turnover time" of the motions.

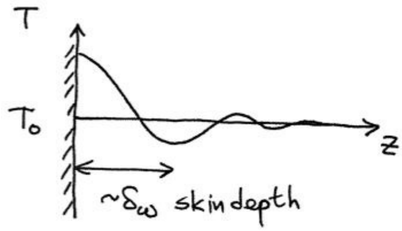


FIGURE 18. Temperature perturbation with given frequency $\omega$ penetrates $\sim$ a skin depth $\delta_\omega$ into heat-conducting medium, as per (5.76).

of (5.48) can be sought in the form

$$T(t,z) = \sum_\omega \hat{T}(\omega,z)e^{-i\omega t}, \tag{5.73}$$

where $\hat{T}(\omega,z)$ must satisfy

$$-i\omega\hat{T} = D_T\frac{\partial^2\hat{T}}{\partial z^2}, \quad \hat{T}(\omega,z=0)=\hat{T}_0(\omega), \quad \hat{T}(\omega,z=\infty)=0. \tag{5.74}$$

The last condition is the assumption that temperature variations decay at infinity, i.e., far away from the source of the disturbance. The solution is

$$\hat{T}(\omega,z) = C_1e^{ikz} + C_2e^{-ikz}, \quad k = (1+i)\sqrt{\frac{|\omega|}{2D_T}}, \tag{5.75}$$

where $C_1 = \hat{T}_0(\omega)$ and $C_2 = 0$ to satisfy the boundary conditions at $z=0$ and $z=\infty$. Finally, from (5.73),

$$\boxed{T(t,z) = \sum_\omega \hat{T}_0(\omega)\exp\left[-i\left(\omega t - \frac{z}{\delta_\omega}\right) - \frac{z}{\delta_\omega}\right], \quad \delta_\omega = \sqrt{\frac{2D_T}{|\omega|}}}, \tag{5.76}$$

where $\delta_\omega$ is the typical scale on which temperature perturbations with frequency $\omega$ decay, known as the *skin depth*—the further away from the boundary (and the higher the frequency), the more feeble is the temperature variation that manages to penetrate there (Fig. 18). Note that it also arrives to $z>0$ with a time delay $\Delta t = z/\delta_\omega\omega$.

This was an example of "relaxation to equilibrium" effectively occurring in space rather than in time.

You see that once we have a diffusion equation for heat or momentum, solving it—and, therefore, working out how systems return (or strive) to global equilibrium—becomes a problem in applied mathematics rather than in physics (although interpreting the answer still requires some physical insight; see Eßler 2009, Magorrian 2017, Lukas 2019). Returning to physics, the key piece of unfinished business that remains is to calculate the diffusion coefficients $D_T$ and $\nu$ (or $\varkappa$ and $\eta$) based on some theory of particle motion and collisions in an ideal gas (and we will restrict these calculations to ideal gas only).

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### 5.7. *Diffusion*

Before I make good on my promise of a proper kinetic calculation, it is useful to discuss what fundamental property of moving particles in a collisional gas the diffusion equations encode.

Let us forget about transport equations for a moment, consider an ideal-gas system and imagine that there is a sub-population of particles in this gas, with number density $n^*$, that carry some identifiable property: e.g., they might be labelled in some way (e.g., be particles of a different species than the rest). Non-rigorously, I will argue that $n^*$ might also be the mean energy or momentum density, and so the evolution equation for $n^*$ that we are about to derive should have the same form as the evolution equations for the mean momentum or energy density (temperature) of the gas.

### 5.7.1. *Derivation of the Diffusion Equation*

Suppose that at time $t$, the mean number density of the labelled particles at the location $z$ is $n^*(t, z)$ (we will work in 1D, assuming that only in the $z$ direction is there a macroscopic variation of $n^*$). What will it be at the same location after a (short) time $\Delta t$? During that time, some particles will move from $z$ to other places and other particles will arrive to $z$ from elsewhere. Therefore,

$$n^*(t + \Delta t, z) = \langle n^*(t, z - \Delta z)\rangle \,, \tag{5.77}$$

where $z - \Delta z$ are positions where the particles that arrive to $z$ at $t + \Delta t$ were at time $t$ and the average is over all these individual particle displacements ($\Delta z$ is a random variable). *This is the essence of "transport": the particle density, or, more generally, some quantity carried by particles, is brought ("transported") to a given location at a given time by particles arriving at that location at that time from elsewhere, so the mean density at $z$ and $t + \Delta t$ is determined by what the density was at $t$ in all those earlier particle locations.*

Let us take $\Delta t$ to be small enough so the corresponding particle displacements are much smaller than the scale of spatial variation of $n^*(z)$, viz.,

$$\Delta z \ll \left(\frac{1}{n^*}\frac{\partial n^*}{\partial z}\right)^{-1}. \tag{5.78}$$

Then we can Taylor-expand (5.77) in small $\Delta z$:

$$n^*(t + \Delta t, z) = \left\langle n^*(t, z) - \Delta z\,\frac{\partial n^*}{\partial z} + \frac{\Delta z^2}{2}\frac{\partial^2 n^*}{\partial z^2} + \dots\right\rangle \approx n^*(t, z) + \frac{\langle\Delta z^2\rangle}{2}\frac{\partial^2 n^*}{\partial z^2}, \tag{5.79}$$

where $\langle\Delta z\rangle = 0$ has been assumed (no mean motion in the $z$ direction; **Exercise**: work out what happens when $\langle\Delta z\rangle = u_z \neq 0$). Rearranging this equation, we get

$$\frac{n^*(t + \Delta t, z) - n^*(t, z)}{\Delta t} = \frac{\langle\Delta z^2\rangle}{2\Delta t}\frac{\partial^2 n^*}{\partial z^2}. \tag{5.80}$$

In the limit $\Delta t \to 0$, we find that $n^*$ satisfies a diffusion equation, similar to (5.48) and (5.49):

$$\boxed{\frac{\partial n^*}{\partial t} = D\,\frac{\partial^2 n^*}{\partial z^2}, \quad D = \lim_{\Delta t\to 0}\frac{\langle\Delta z^2\rangle}{2\Delta t}}\,, \tag{5.81}$$

*assuming that the limit exists and so $D$ is finite.*

### 5.7.2. *Random-Walk Model*

So, is $D$ finite? It is important to understand that "$\Delta t \to 0$" here means that $\Delta t$ is small compared to the time scales on which the diffusive evolution of $n^*$ occurs ($\Delta t \ll \tau_{\rm diff}$ in the notation of §5.6.3), but it can still be a long time compared to the collision time, $\Delta t \gg \tau_{\rm c}$. Let us model particle motion as a succession of free flights, each lasting for a time $\tau_{\rm c}$ and followed by a random kick—a collision with another particle—as a result of which the direction of the particle's motion in the $z$ direction may be reversed. Mathematically, we may write this model for particle displacements as follows

$$\Delta z = \sum_{i=1}^{N}\delta z_i, \tag{5.82}$$

where $\delta z_i$ are independent random displacements with mean $\langle\delta z_i\rangle = 0$ and variance $\langle\delta z_i^2\rangle = \lambda_{\rm mfp}^2$, and $N = \Delta t/\tau_{\rm c}$ is the number of collisions over time $\Delta t$. By the Central Limit Theorem (see, e.g., Sinai 1992), in the limit $N \to \infty$, the quantity

$$X = \sqrt{N} \left( \frac{1}{N} \sum_{i=1}^{N} \delta z_i - \langle \delta z_i \rangle \right) \tag{5.83}$$

will have a normal (Gaussian) distribution with zero mean and variance $\langle \delta z_i^2 \rangle - \langle \delta z_i \rangle^2 = \lambda_{\rm mfp}^2$:

$$f(X) = \frac{1}{\lambda_{\rm mfp}\sqrt{2\pi}}\, e^{-X^2/2\lambda_{\rm mfp}^2}. \tag{5.84}$$

Since $\varDelta z = X\sqrt{N}$, we conclude that, for $N = \varDelta t/\tau_{\rm c} \gg 1$,

$$D = \frac{\langle \varDelta z^2 \rangle}{2\varDelta t} = \frac{\langle X^2 \rangle}{2\tau_{\rm c}} = \frac{\lambda_{\rm mfp}^2}{2\tau_{\rm c}}, \tag{5.85}$$

so we recover the dimensional guess (5.62), up to a numerical factor, of course.

The model of the particle motion that we have used to obtain this result—a sequence of independent random increments—is known as *Brownian motion*, or *random walk*, and describes random meandering of a particle being bombarded by other particles of the gas and thus undergoing a sequence of random kicks. The density of such particles—or of any quantity they carry, such as energy or momentum—always satisfies a diffusion equation, as follows from the above derivation (in §6.9, the full kinetic theory of Brownian particles is developed more rigorously and systematically).

When used to describe a diffusive spreading of an admixture of particles of a distinct species in an ambient gas, (5.81) is called *Fick's law*. In the expression (5.85) for the diffusion coefficient, $\lambda_{\rm mfp}$ and $\tau_{\rm c}$ are the mean free path and the collision time of the labelled species (which, if this species has different mass than the ambient one, are not the same as the ambient mean free path and collision time; see Exercise 4.3).

If we were to use the model above to understand transport of energy or momentum, while this is fine qualitatively, we ought to be cognizant of an important nuance. Implicitly, if we treat $n^*$ as energy density ($nc_1T$) or momentum density ($mnu_x$) and carry out exactly the same calculation, we are assuming that particles that have random-walked through many collisions from $z - \varDelta z$ to $z$ have not, through all these collisions, changed their energy or momentum. This is, of course, incorrect—in fact, in each collision, energy and momentum are exchanged and so the velocity of each particle receives a random kick uncorrelated with the particle's previous history. Thus, the particle random-walks not just in position space $z$ but also in velocity space $\boldsymbol{v}$. The reason the above calculation is still fine is that we can think of the particles it describes not literally as particles but as units of energy or momentum random-walking from place to place—and also from particle to particle!—and thus effectively diffusing from regions with higher average $u_x$ or $T$ to regions with lower such averages.

Thus, we have argued that the diffusion equation—(5.81), (5.48) or (5.49)—is a macroscopic manifestation of particles (or energy, or momentum) random walking and, roughly speaking, covering distances that scale as $\sqrt{t}$ with the time it takes to cover them. This would suggest that an initial spot of concentration of a particle admixture, energy or momentum would spread in space as $\sqrt{t}$. This is indeed the case, as we already inferred from the solution to the initial-value problem worked out in §5.6.1.

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## 6. Kinetic Calculation of Transport Coefficients

### 6.1. *A Nice but Dodgy Derivation*

[Literature: Blundell & Blundell (2009), §9]

#### 6.1.1. *Viscosity*

Given a shear flow profile, $u_x(z)$, we wish to calculate the momentum flux $\varPi_{zx}$ through the plane defined by a fixed value of the coordinate $z$ (Fig. 19). The number of particles

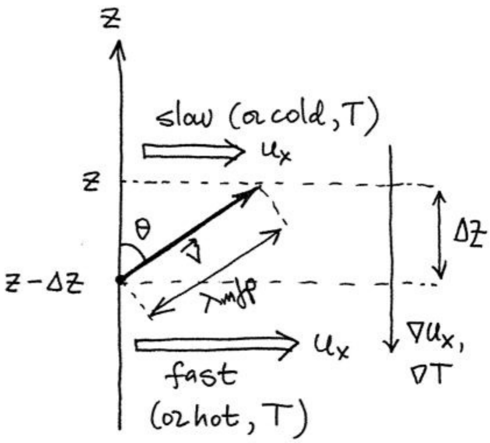


FIGURE 19. Physics of transport: particles wander from faster-moving (or hotter) regions to slower (or colder) ones, bring with then extra momentum (or energy). This gives rise to net momentum (or heat) flux and so to the viscosity (thermal conductivity) of the gas.

with velocity $\boldsymbol{v}$ that cross that plane per unit time per unit area is given by (3.2):

$$d\Phi(\boldsymbol{v}) = nv_z f(\boldsymbol{v})d^3\boldsymbol{v} = nv^3 f(v)dv\cos\theta\sin\theta d\theta d\phi. \tag{6.1}$$

These particles have travelled the distance $\lambda_{\rm mfp}$ since their last collision—i.e., since they last "communicated" with the gas as a collective. This was at the position $z - \Delta z$, where $\Delta z = \lambda_{\rm mfp}\cos\theta$ (because they are flying at angle $\theta$ to the $z$ axis). But, since $u_x$ is a function of $z$, the mean momentum of the particles at $z - \Delta z$ is different than it is at $z$ and so a particle that last collided at $z - \Delta z$ brings with it to $z$ some extra momentum:

$$\Delta p = mu_x(z - \Delta z) - mu_x(z) \approx -m\frac{\partial u_x}{\partial z}\Delta z = -m\frac{\partial u_x}{\partial z}\lambda_{\rm mfp}\cos\theta, \tag{6.2}$$

assuming that $\Delta z \ll l$ ($l$ is the scale of variation of $u_x$). The flux of momentum through $z$ is then simply

$$\Pi_{zx} = \int d\Phi(\boldsymbol{v})\Delta p = -mn\frac{\partial u_x}{\partial z}\lambda_{\rm mfp}\underbrace{\int_0^\infty dv\, v^3 f(v)}_{=\langle v\rangle/4\pi}\underbrace{\int_0^\pi d\theta\cos^2\theta\sin\theta}_{=2/3}\underbrace{\int_0^{2\pi}d\phi}_{=2\pi}$$
$$= -\frac{1}{3}mn\lambda_{\rm mfp}\langle v\rangle\frac{\partial u_x}{\partial z}. \tag{6.3}$$

Note that, unlike in our effusion (§3) or pressure (§1.4) calculations, the integral is over all $\theta$ because particles come from $z - \Delta z$, where $\Delta z = \lambda_{\rm mfp}\cos\theta$ can be positive or negative.

Comparing (6.3) with (5.40), we read off the expression for dynamical viscosity:

$$\boxed{\eta = \frac{1}{3}mn\lambda_{\rm mfp}\langle v\rangle = \frac{2}{3\sqrt{\pi}}mn\lambda_{\rm mfp}v_{\rm th} = \frac{2}{3\sigma}\sqrt{\frac{2mk_{\rm B}T}{\pi}}}\,. \tag{6.4}$$

We have recovered the dimensional guess (5.62), with a particular numerical coefficient (which is, however, wrong, as I am about to explain). Note that the assumption $\Delta z \sim \lambda_{\rm mfp} \ll l$ is justified *a posteriori:* once we have (6.4), we can confirm scale separation as in §5.6.3.

The last expression in (6.4), to obtain which we used (4.5) and (2.21), emphasises the fact that the dynamical viscosity depends on the temperature but not the number density of the gas.

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**Exercise 6.1.** What is going on physically? Why does it make sense that the rate of momentum transport should be independent of the density of particles that transport it? Robert Boyle discovered this in 1660 when he put a pendulum inside a vessel from which he proceeded to pump out the air. The rate at which the pendulum motion was damped did not change.

If Boyle had had a really good vacuum pump and continued pumping the air out, at what pressure would have he started detecting a change in the pendulum's damping rate? Below that pressure, estimate the momentum flux from the pendulum, given the pendulum's typical velocity $u$ and any other parameters that you might reasonably expect to know.

---

### 6.1.2. *Thermal Conductivity*

In order to obtain the heat flux $J_z$, given some temperature profile $T(z)$, we go through a completely analogous calculation: particles that arrive at $z$ after having last experienced a collision at $z - \mathit{\Delta} z$ bring to $z$ some extra energy:

$$\mathit{\Delta} E = c_1 T(z - \mathit{\Delta} z) - c_1 T(z) \approx -c_1 \frac{\partial T}{\partial z}\, \lambda_{\rm mfp} \cos\theta. \tag{6.5}$$

Therefore, the flux of energy (heat flux) is

$$J_z = \int \mathrm{d}\mathit{\Phi}(\boldsymbol{v}) \mathit{\Delta} E = -\frac{1}{3}\, n c_1 \lambda_{\rm mfp} \langle v\rangle \frac{\partial T}{\partial z}, \tag{6.6}$$

whence, upon comparison with (5.39), we infer the thermal conductivity:

$$\boxed{\varkappa = \frac{1}{3}\, n c_1 \lambda_{\rm mfp} \langle v\rangle = \frac{2}{3\sqrt{\pi}}\, n c_1 \lambda_{\rm mfp} v_{\rm th} = \frac{2c_1}{3\sigma}\sqrt{\frac{2k_{\rm B}T}{\pi m}}}\,. \tag{6.7}$$

This again is consistent with the dimensional expression (5.62).

---

**Exercise 6.2. Fick's Law of Diffusion.** Given the number density $n^*(z)$ and the mean free path $\lambda_{\rm mfp}$ of an admixture of labelled particles, as well as the temperature of the ambient gas, calculate the flux of the labelled species, $\mathit{\Phi}_z^*$, and derive Fick's Law of Diffusion (5.81).

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### 6.1.3. *Why This Derivation is Dodgy*

Our new expressions (6.4) and (6.7) for the transport coefficients and their derivation *look* more quantitative and systematic than what we had before, but in fact they are not. It is useful to understand why that is, in order to appreciate the need for, and the structure of, the better derivation that is to follow.

Much of the appearance of rigour in the derivation of (6.4) and (6.7) came from taking into account the fact that particles ending up at location $z$ at time $t$ might have travelled at an angle to the $z$ axis. Integrating over the resulting combination of sines and cosines produced numerical factors that had the veneer of quantitative precision. However, while precisely integrating over the particles' angle distribution, we blithely assumed that they all had travelled exactly the same distance $\lambda_{\rm mfp}$ between collisions and carried exactly the same excess momentum ($\mathit{\Delta} p$) and energy ($\mathit{\Delta} E$)—but surely all of these things must in fact depend on the particles' velocities, which are random variables and so have to be averaged over properly? To illustrate the imprecise nature of these assumptions, imagine that instead of what we did, we had assumed that all particles travelled the same time $\tau_{\rm c}$ between collisions. Then we would have had to replace $\lambda_{\rm mfp} \to v\tau_{\rm c}$ in our calculations, leading to

$$\frac{\eta}{mn} = \frac{\varkappa}{nc_1} = \frac{1}{3}\langle v^2\rangle\tau_c = \frac{1}{2}\,v_{th}^2\tau_c = \frac{1}{2}\,\lambda_{mfp}v_{th}. \tag{6.8}$$

This has the same dependence on $\lambda_{mfp}$ and $v_{th}$ as our previous attempts, but a different numerical coefficient (which is as wrong—or as qualitatively irrelevant—as all the other ones that we have calculated so far).

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You might object that the assumption of a constant $\lambda_{mfp}$ was in fact more plausible: indeed, we saw in §4.3 that $\lambda_{mfp}$, at least when estimated very roughly, was independent of the particles' velocity (except via possible $v$ dependence of the collisional cross section $\sigma$, for "squishy" particles). On the other hand, imagining the extreme case of a particle sitting still, one might argue that it would remain still until hit by some other particle, after some characteristic collision time $\tau_c$, so perhaps a constant $\tau_c$, as in (6.8), is not an entirely unreasonable model either. The correct $v$ dependence of $\lambda_{mfp}$, or, equivalently, of the collision time $\tau_c$, can be worked out systematically for any particular model of collisions: e.g., for the "hard-spheres" model, $\tau_c \sim$ const when $v \ll v_{th}$ and $\tau_c \sim \lambda_{mfp}/v$, $\lambda_{mfp} \sim$ const when $v \gg v_{th}$, with a more nontrivial behaviour in between the two limits (see, e.g., Dellar 2015). This is because the faster particles can be thought of as rushing around amongst an almost immobile majority population, as envisioned by the arguments of §4, whereas the slower ones are better modelled as sitting ducks waiting to be hit. Thus, both $\lambda_{mfp} =$ const and $\tau_c =$ const are plausible, but not quantitatively correct, simplifications for the majority of the particles (for which $v \sim v_{th}$).

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Thus, the derivation given in this section is in fact no more rigorous then the random-walk model of §5.7.2 or even the dimensional estimate of §5.6.2—although it does highlight the essential fact that we need some sort of kinetic (meaning based on the particles' velocity distribution) calculation of the fluxes.

Another, somewhat more formalistic, objection to our last derivation is that the homogeneous Maxwellian $f(v)$ was used, despite the fact that we had previously made quite a lot of fuss about only having a *local* Maxwellian $F(t, \boldsymbol{r}, \boldsymbol{v})$ [see (5.10)] depending on $z$ via $T(z)$ and $u_x(z)$. In fact, this was OK because the scale of inhomogeneities was long ($l \gg \lambda_{mfp}$) and the flow velocity small ($u_x \ll v_{th}$), but we certainly did not set up a systematic expansion around a homogeneous distribution that might have justified this approach.

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You will find some further critique of the derivation above, as well as the quantitatively correct formulae for the transport coefficients, in Blundell & Blundell (2009), §9.4. The derivation of these formulae can be found, e.g., in Chapman & Cowling (1991).

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Clearly, if I am to claim that I really can do better than the unapologetically qualitative arguments in §5, I must develop a more systematic algorithm for calculating transport coefficients. I shall do this now and, in the process, we will learn how to solve (kinetic) problems involving scale separation—a useful piece from the toolbox of theoretical physics.

### 6.2. *Kinetic Expressions for Fluxes*

Let us go back to basics. Suppose we know the particle distribution $F(z, \boldsymbol{v})$ (we continue to stick to the 1D case). The fluxes of momentum and energy are

$$\Pi_{zx}(z) = \int d^3\boldsymbol{v}\, mv_x \cdot v_z \cdot F(z, \boldsymbol{v}), \tag{6.9}$$

$$J_z(z) = \int d^3\boldsymbol{v}\, \frac{mv^2}{2} \cdot v_z \cdot F(z, \boldsymbol{v}) \tag{6.10}$$

(in the latter expression, I took $\boldsymbol{u} = 0$ for simplicity, a restriction that will be lifted in §6.4.3). But if $F$ is a local Maxwellian,

$$F_{\rm M}(z, \boldsymbol{v}) = \frac{n}{[\sqrt{\pi} v_{\rm th}(z)]^3} \exp\left\{-\frac{[v_x - u_x(z)]^2 + v_y^2 + v_z^2}{v_{\rm th}^2(z)}\right\}, \quad v_{\rm th}(z) = \sqrt{\frac{2k_{\rm B}T(z)}{m}}, \tag{6.11}$$

then $\Pi_{zx} = 0$ and $J_z = 0$ because they both have a single power of $v_z$ under the integral and $F_{\rm M}$ is even in $v_z$! This means that non-zero fluxes come from the distribution function in fact *not* being *exactly* a local Maxwellian:

$$F(z, \boldsymbol{v}) = F_{\rm M}(z, \boldsymbol{v}) + \delta F(z, \boldsymbol{v}), \tag{6.12}$$

and we must now find $\delta F$.

In order to do this, we need an *evolution equation* for $F$, the argument for a local Maxwellian (§5.2) is no longer enough.

## 6.3. *Kinetic Equation*

The simplest derivation of the kinetic equation goes as follows. The particles found at location $\boldsymbol{r}$ with velocity $\boldsymbol{v}$ at time $t + \Delta t$ are the particles moving at velocity $\boldsymbol{v}$ that arrived to this location from $\boldsymbol{r} - \boldsymbol{v}\Delta t$, where they were at time $t$, plus those that got scattered into this $\boldsymbol{v}$ by collisions that they had experienced during the time interval $[t, t + \Delta t]$, at the location $\boldsymbol{r}$:

$$F(t + \Delta t, \boldsymbol{r}, \boldsymbol{v}) = F(t, \boldsymbol{r} - \boldsymbol{v}\Delta t, \boldsymbol{v}) + \Delta F_{\rm c} \approx F(t, \boldsymbol{r}, \boldsymbol{v}) - \boldsymbol{v} \cdot \boldsymbol{\nabla} F(t, \boldsymbol{r}, \boldsymbol{v})\Delta t + \Delta F_{\rm c}, \tag{6.13}$$

where we have expanded in $\boldsymbol{v}\Delta t$ assuming small enough $\Delta t$, viz., $v\Delta t \ll |\boldsymbol{\nabla} \ln F|^{-1}$. Dividing through by $\Delta t$ and taking the limit $\Delta t \to 0$, we get the *kinetic equation:*

$$\boxed{\frac{\partial F}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} F = C[F]}\,, \tag{6.14}$$

where the right-hand side, $C[F] = \lim_{\Delta t \to 0} \Delta F_{\rm c}/\Delta t$, is called the *collision operator*, whereas the left-hand side expresses conservation of particle density in phase space: indeed, our equation can be written as $\partial F/\partial t = -\boldsymbol{\nabla} \cdot (\boldsymbol{v}F) + C[F]$, where $\boldsymbol{v}F$ is the flux of particles with velocity $\boldsymbol{v}$.

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**Exercise 6.3. Kinetic Equation for a Plasma.** We have assumed that no forces act on particles, apart from collisions. Work out the form of the kinetic equation if some external force $m\boldsymbol{a}$ acts on each particle, e.g., gravity $\boldsymbol{a} = \boldsymbol{g}$, or Lorentz force $\boldsymbol{a} = (q/m)(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}/c)$ ($q$ is the particle charge). The kinetic equation for the latter case is the Vlasov–Landau equation describing an ionised particle species in a plasma (see, e.g., lecture notes by Schekochihin 2025, and references therein).

---

The kinetic equation (6.14) might appear rather less than satisfactory as we have not specified what $C[F]$ is. Thinking about what it might be is depressing as it is clearly quite a complicated object:
—collisions leading to a change in the local number of particles with velocity $\boldsymbol{v}$ must have involved particles that had other velocities $\boldsymbol{v}'$ before they collided, so $C[F]$ is likely to be a integral operator depending on $F(t, \boldsymbol{r}, \boldsymbol{v}')$ integrated over a range of $\boldsymbol{v}'$;
—assuming predominantly binary collisions, $C[F]$ is also likely to be a quadratic (and so nonlinear!) operator in $F$ because the probability of getting a particle with velocity $\boldsymbol{v}$ after a collision must depend on the joint probability of two particles with some suitable velocities meeting.

In §6.5, I will happily avoid these complications by introducing a very simple model of $C[F]$,[25] but first let us see what can be done without knowing the explicit form of $C[F]$ (in the process, we will also learn of some important properties that any collision operator must have).

### 6.4. *Conservation Laws and Fluid Equations*

The kinetic equation (6.14) in principle contains full information about the evolution of the system, so we ought to be able to recover from it the conservation equations (5.18) and (5.27), which I originally derived on general grounds.

There are three conserved quantities in our system: the number of particles, their total momentum and energy. The game plan now is to work out the evolution equations for the densities of these quantities: particle number density $n$, momentum density $mn\boldsymbol{u}$, and internal-energy density $(3/2)nk_{\rm B}T$, and hence find how the flow velocity $\boldsymbol{u}$ and temperature $T$ evolve. I shall do this by taking moments of (6.14).

#### 6.4.1. *Number Density*

The zeroth moment of (6.14) is

$$\frac{\partial n}{\partial t} = \int \mathrm{d}^3\boldsymbol{v}\,\frac{\partial F}{\partial t} = \int \mathrm{d}^3\boldsymbol{v}\,(-\boldsymbol{v}\cdot\boldsymbol{\nabla}F + C[F]) \\ = -\boldsymbol{\nabla}\cdot\underbrace{\int \mathrm{d}^3\boldsymbol{v}\,\boldsymbol{v}F}_{=n\boldsymbol{u},\ \text{see (5.5)}} + \underbrace{\int \mathrm{d}^3\boldsymbol{v}\,C[F]}_{=0}. \tag{6.15}$$

The second term vanishes because, whatever the explicit form of the collision operator is, it cannot lead to any change in the number of particles—*elastic collisions conserve particle number*:[26]

$$\int \mathrm{d}^3\boldsymbol{v}\,C[F] = 0. \tag{6.16}$$

Thus, we arrive at the *continuity equation*

$$\boxed{\frac{\partial n}{\partial t} + \boldsymbol{\nabla}\cdot(n\boldsymbol{u}) = 0}\,, \tag{6.17}$$

which you have already had the opportunity to derive on general particle-conservation grounds in Exercise 5.2 [see (5.23)]. It is good to know that our kinetic equation allows us to recover such non-negotiable results. We are about to see that it will also allow us to recover (5.35) and (5.37), but this time we will be able to work out explicitly what $\boldsymbol{\mathit{\Pi}}^{\rm (viscous)}$ and $\boldsymbol{J}$ are.

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[25]See, e.g., lecture notes by Dellar (2015) for the derivation of Boltzmann's full collision operator. See also §6.9.2 for a simple derivation of a collision operator describing a particular kind of particles.

[26]In (6.13), $\Delta F_{\rm c}$ represents collisions between particles at the point $\boldsymbol{r}$ in space. The only effect of these collisions is a redistribution of particle velocities—any movements of particles between different points in space are accounted for in the $\boldsymbol{v}\cdot\boldsymbol{\nabla}F$ term. Therefore, $\Delta F_{\rm c}$ cannot change the total number of particles at $\boldsymbol{r}$ and so $\int \mathrm{d}^3\boldsymbol{v}\,\Delta F_{\rm c} = 0$. Similar logic applies to the conservation of momentum (6.19) and energy (6.31).

6.4.2. *Momentum Density*

The first moment of (6.14) is[27]

$$\frac{\partial}{\partial t} mn\boldsymbol{u} = \int \mathrm{d}^3\boldsymbol{v}\, m\boldsymbol{v}\, \frac{\partial F}{\partial t} = \int \mathrm{d}^3\boldsymbol{v}\, m\boldsymbol{v}\,(-\boldsymbol{v}\cdot\boldsymbol{\nabla} F + C[F])$$
$$= -\boldsymbol{\nabla}\cdot\int \mathrm{d}^3\boldsymbol{v}\, m\boldsymbol{v}\boldsymbol{v}F + \underbrace{\int \mathrm{d}^3\boldsymbol{v}\, mv_x C[F]}_{=0}. \tag{6.18}$$

Similarly to (6.15), the collisional term vanishes because, again, whatever the explicit form of the collision operator might be, it cannot lead to any change in the mean momentum of particles—*elastic collisions conserve momentum:*

$$\int \mathrm{d}^3\boldsymbol{v}\, m\boldsymbol{v}\, C[F] = 0. \tag{6.19}$$

We now have to do some technical work separating the mean flow from the random motions, $\boldsymbol{v} = \boldsymbol{u} + \boldsymbol{w}$:

$$\frac{\partial}{\partial t} mn\boldsymbol{u} = -\boldsymbol{\nabla}\cdot\int \mathrm{d}^3\boldsymbol{w}\, m(\boldsymbol{u}+\boldsymbol{w})(\boldsymbol{u}+\boldsymbol{w})F$$
$$= -\boldsymbol{\nabla}\cdot\Bigg[m\boldsymbol{u}\boldsymbol{u}\underbrace{\int \mathrm{d}^3\boldsymbol{w}\, F}_{=n} + \underbrace{\int \mathrm{d}^3\boldsymbol{w}\, m\,(\boldsymbol{u}\boldsymbol{w}+\boldsymbol{w}\boldsymbol{u})\,F}_{=0\text{ by definition of }\boldsymbol{w}} + \int \mathrm{d}^3\boldsymbol{w}\, m\boldsymbol{w}\boldsymbol{w}F\Bigg]$$
$$= \underbrace{-m\boldsymbol{u}\boldsymbol{\nabla}\cdot(n\boldsymbol{u})}_{\substack{= m\boldsymbol{u}\,\frac{\partial n}{\partial t},\\ \text{from (6.17)}}} - mn\boldsymbol{u}\cdot\boldsymbol{\nabla}\boldsymbol{u} - \underbrace{\boldsymbol{\nabla}\cdot\int \mathrm{d}^3\boldsymbol{w}\, m\boldsymbol{w}\boldsymbol{w}F_{\mathrm{M}}}_{\substack{=\boldsymbol{\nabla}\frac{1}{3}\int \mathrm{d}^3\boldsymbol{w}\, mw^2F_{\mathrm{M}}\\ =\boldsymbol{\nabla}P,\\ \text{from (1.29)}}} - \boldsymbol{\nabla}\cdot\underbrace{\int \mathrm{d}^3\boldsymbol{w}\, m\boldsymbol{w}\boldsymbol{w}\,\delta F}_{\substack{\equiv\boldsymbol{\Pi}\\ \text{viscous stress,}\\ \text{cf. (6.9)}}}. \tag{6.20}$$

Now combining the left-hand side of (6.20) with the first term on its right-hand side, we arrive at the evolution equation for the mean velocity of the gas:

$$\boxed{mn\left(\frac{\partial\boldsymbol{u}}{\partial t} + \boldsymbol{u}\cdot\boldsymbol{\nabla}\boldsymbol{u}\right) = -\boldsymbol{\nabla}P - \boldsymbol{\nabla}\cdot\boldsymbol{\Pi}}\,. \tag{6.21}$$

Thus, we have recovered (5.35), which, when specialised to the case of a shear flow with 1D spatial dependence, $\boldsymbol{u} = u_x(z)\hat{\boldsymbol{x}}$, gives us back the momentum-conservation

[27] The first term in the last expression here is the first instance where I use the "direct product" of vectors, which may be unfamiliar to some. So, when two vectors appear next to each other, without any symbol in between, e.g., $\boldsymbol{u}\boldsymbol{w}$, this means a matrix whose elements are $u_iw_j$ (in contrast, $\boldsymbol{u}\cdot\boldsymbol{w} = u_iw_i$, a scalar quantity, which is the trace of the matrix $\boldsymbol{u}\boldsymbol{w}$). If the two vectors are different, the matrix is not symmetric, and then the order in which the vectors appear matters. Operations such as the dot product then work in the usual way: for a matrix $\mathsf{A}$ whose elements are $a_{ij}$, $\boldsymbol{v}\cdot\mathsf{A}$ is a vector whose $j$-th element is $v_ia_{ij}$ (using Einstein notation for the summation over the repeated index $i$), but $\mathsf{A}\cdot\boldsymbol{v} \leftrightarrow a_{ji}v_i$, and so, $\boldsymbol{\nabla}\cdot\mathsf{A} \leftrightarrow \partial_i a_{ij}$, $\boldsymbol{\nabla}\cdot\boldsymbol{u}\boldsymbol{w} \leftrightarrow \partial_i u_i w_j$. My convention is that, in vector notation, the convolution (summation over the repeated index) is between the indices closest to the dot on both sides, and the derivatives act on everyting that is to the right of them unless brackets are used to override that: $\boldsymbol{\nabla}\cdot\boldsymbol{u}\boldsymbol{w}$ is the same as $\boldsymbol{\nabla}\cdot(\boldsymbol{u}\boldsymbol{w})$, but in $(\boldsymbol{\nabla}\cdot\boldsymbol{u})\boldsymbol{w}$, the derivative only acts on $\boldsymbol{u}$.

equation (5.27):

$$mn\frac{\partial u_x}{\partial t} = -\frac{\partial \Pi_{zx}}{\partial z}. \tag{6.22}$$

The momentum flux, which will become viscous stress once we are done with this extended calculation, is, by definition, the matrix

$$\Pi_{ij} = \int \mathrm{d}^3\boldsymbol{w}\, m w_i w_j \delta F. \tag{6.23}$$

The element of this matrix already familiar to us from previous derivations is

$$\boxed{\Pi_{zx} = m\int \mathrm{d}^3\boldsymbol{w}\, w_z w_x \delta F}\,. \tag{6.24}$$

Note that (6.21) teaches us that we cannot, technically speaking, restrict the gas flow just to $\boldsymbol{u} = u_x(z)\hat{\boldsymbol{x}}$ (or to zero) and density to $n = \text{const}$ if we also want there to be a non-constant temperature profile $T = T(z)$. Indeed, $P = nk_{\mathrm{B}}T$, so a temperature gradient in the $z$ direction will produce a pressure gradient in the same direction and that will drive a flow $u_z$. The flow will then change the density of the gas according to (6.17), that will change $\boldsymbol{\nabla}P$, etc.—it is clear that, whatever the detailed dynamics, the system will strive towards pressure balance, $\boldsymbol{\nabla}P = 0$, and thus we will end up with

$$\frac{\boldsymbol{\nabla}n}{n} = -\frac{\boldsymbol{\nabla}T}{T}, \tag{6.25}$$

so there will be a density gradient to compensate the temperature gradient. This will normally happen much faster than the heat or momentum diffusion because the pressure-gradient force acts dynamically, without being limited by the smallness of the collisional mean free path.[28] Therefore, as the slower evolution of $T$ due to heat diffusion proceeds at its own snail pace, we can assume $n$ to be adjusting instantaneously to satisfy (6.25).

---

The flows that are required to effect this adjustment are very small: from (6.17), we can estimate

$$\boldsymbol{\nabla}\cdot\boldsymbol{u} \sim \frac{1}{n_0}\frac{\partial \delta n}{\partial t} \sim \frac{\partial}{\partial t}\frac{\delta T}{T_0} \sim \frac{D_T}{l^2}\frac{\delta T}{T_0} \sim \frac{v_{\mathrm{th}}\lambda_{\mathrm{mfp}}}{l^2}\frac{\delta T}{T_0} \quad \Rightarrow \quad \frac{u_z}{v_{\mathrm{th}}} \sim \frac{\lambda_{\mathrm{mfp}}}{l}\frac{\delta T}{T_0}, \tag{6.26}$$

where $\delta n$ and $\delta T$ are typical sizes of the density and temperature perturbations from their constant spatial means $n_0$ and $T_0$; note that $\delta n/n_0 \sim \delta T/T_0$ because of (6.25). In principle, nothing stops the shear flow $u_x(z)$ from being much greater than this, even if still subsonic ($u_x \ll v_{\mathrm{th}}$).

---

### 6.4.3. *Energy Density*

The second moment of $F$ corresponding to energy contains both the bulk and internal motion because we are keeping the flow velocity $\boldsymbol{u}$ in this calculation: as in (5.6),

$$\langle E\rangle = \int \mathrm{d}^3\boldsymbol{v}\,\frac{mv^2}{2}F = \frac{mnu^2}{2} + \int \mathrm{d}^3\boldsymbol{w}\,\frac{mw^2}{2}F = \frac{mnu^2}{2} + \frac{3}{2}nk_{\mathrm{B}}T. \tag{6.27}$$

The first term is the kinetic energy of the mean motion and the second is the internal energy, related to temperature in the usual way, given by (5.11). Note that the deviation $\delta F$ of $F$ from the local Maxwellian $F_{\mathrm{M}}$ cannot contribute to energy—or, indeed, to the number density or the flow velocity. This is because the local Maxwellian equilibrium is

[28] Namely, pressure gradients will be wiped out on the time scale $\sim l/v_{\mathrm{th}}$ of sound propagation across the typical scale $l$ of any (briefly) arising pressure inhomogeneity.

*defined* by the three quantities $n$, $\boldsymbol{u}$ and $T$ and so any changes in $n$, $\boldsymbol{u}$ and $T$ that do occur can always be absorbed into the local Maxwellian $F_{\rm M}$.[29]

---

Namely, consider any arbitrary pdf $F$. Let $F_{\rm M}$ be a local Maxwellian [see (5.10)] such that its density $n$, mean velocity $\boldsymbol{u}$ and mean energy $\varepsilon = 3nk_{\rm B}T/2$ are the same as the density, mean velocity and mean energy of $F$ (as defined in §5.1). Then we can always write

$$F = F_{\rm M} + \underbrace{F - F_{\rm M}}_{\equiv\,\delta F}, \tag{6.28}$$

where $\delta F$ contains no particle-, momentum- or energy-density perturbation.

---

The definition (6.27) implies that the rate of change of the internal energy is

$$\frac{\partial}{\partial t}\frac{3}{2}nk_{\rm B}T = \frac{\partial\langle E\rangle}{\partial t} - \frac{\partial}{\partial t}\frac{mnu^2}{2}. \tag{6.29}$$

Let us calculate both of these contributions. The second one will follow from (6.17) and (6.21), but for the first, we shall need the kinetic equation again.

Taking the $mv^2/2$ moment of (6.14), we get

$$\begin{aligned}\frac{\partial\langle E\rangle}{\partial t} &= \int d^3\boldsymbol{v}\,\frac{mv^2}{2}\frac{\partial F}{\partial t} = \int d^3\boldsymbol{v}\,\frac{mv^2}{2}\left(-\boldsymbol{v}\cdot\boldsymbol{\nabla}F + C[F]\right)\\ &= -\boldsymbol{\nabla}\cdot\int d^3\boldsymbol{v}\,\frac{mv^2}{2}\,\boldsymbol{v}F + \underbrace{\int d^3\boldsymbol{v}\,\frac{mv^2}{2}\,C[F]}_{=0}.\end{aligned} \tag{6.30}$$

Similarly to (6.15) and (6.20), the second term vanishes because the collision operator cannot lead to any change in the mean energy of particles—*elastic collisions conserve energy:*

$$\int d^3\boldsymbol{v}\,\frac{mv^2}{2}\,C[F] = 0. \tag{6.31}$$

The first term in (6.30) looks very much like the divergence of the heat flux (6.10), but we must be careful as heat is only the random part of the motions, whereas $\boldsymbol{v}$ now also contains the mean flow $\boldsymbol{u}$. Breaking up $\boldsymbol{v} = \boldsymbol{u} + \boldsymbol{w}$ as before, where $\int d^3\boldsymbol{v}\,\boldsymbol{w}F = 0$, we get

$$\begin{aligned}\frac{\partial\langle E\rangle}{\partial t} &= -\boldsymbol{\nabla}\cdot\Bigg(\boldsymbol{u}\underbrace{\int d^3\boldsymbol{v}\,\frac{mv^2}{2}\,F}_{=\langle E\rangle} + \underbrace{\int d^3\boldsymbol{v}\,\frac{mv^2}{2}\,\boldsymbol{w}F}_{=\int d^3\boldsymbol{w}\,\frac{m|\boldsymbol{u}+\boldsymbol{w}|^2}{2}\,\boldsymbol{w}F}\Bigg)\\ &= -\boldsymbol{\nabla}\cdot\Bigg[\boldsymbol{u}\langle E\rangle + \frac{mu^2}{2}\underbrace{\int d^3\boldsymbol{w}\,\boldsymbol{w}F}_{=0} + \underbrace{\left(\int d^3\boldsymbol{w}\,m\boldsymbol{w}\boldsymbol{w}F\right)}_{=P\mathsf{I}+\boldsymbol{\Pi},\ \text{as in (6.20)}}\cdot\,\boldsymbol{u} + \underbrace{\int d^3\boldsymbol{w}\,\frac{mw^2}{2}\,\boldsymbol{w}F}_{\equiv\boldsymbol{J}\ \text{heat flux}}\Bigg]\\ &= -\boldsymbol{\nabla}\cdot\left[\boldsymbol{u}\left(\frac{mnu^2}{2} + \frac{3}{2}nk_{\rm B}T\right) + \boldsymbol{u}P + \boldsymbol{\Pi}\cdot\boldsymbol{u} + \boldsymbol{J}\right]\end{aligned} \tag{6.32}$$

[29]Note that this implies that the viscous stress tensor (6.23) is traceless.

We have now extracted the heat flux:

$$\boldsymbol{J} = \int \mathrm{d}^3\boldsymbol{w}\, \frac{mw^2}{2}\, \boldsymbol{w}\delta F, \tag{6.33}$$

or, in the familiar 1D form,

$$\boxed{J_z = \int \mathrm{d}^3\boldsymbol{w}\, \frac{mw^2}{2}\, w_z\delta F}\,, \tag{6.34}$$

where only $\delta F$ is left because $\boldsymbol{J} = 0$ for $F = F_\mathrm{M}$, the local Maxwellian distribution being even in $\boldsymbol{w}$ (see §6.2). It remains to mop up the rest of the terms.

Recall that, to get the rate of change of internal energy, we need to subtract from the rate of change of the total energy (6.32) the rate of change of the kinetic energy of the mean motions [see (6.29)]. The latter quantity can be calculated by substituting for $\partial n/\partial t$ and for $mn\partial\boldsymbol{u}/\partial t$ the continuity equation (6.17) and the momentum equation (6.21), respectively:

$$\begin{aligned}\frac{\partial}{\partial t}\frac{mnu^2}{2} &= \frac{mu^2}{2}\frac{\partial n}{\partial t} + mn\boldsymbol{u}\cdot\frac{\partial\boldsymbol{u}}{\partial t}\\ &= -\cancel{\frac{mu^2}{2}\boldsymbol{\nabla}\cdot(n\boldsymbol{u})} - \cancel{mn\boldsymbol{u}\cdot\boldsymbol{\nabla}\frac{u^2}{2}} - \cancel{\boldsymbol{u}\cdot\boldsymbol{\nabla}P} - \cancel{(\boldsymbol{\nabla}\cdot\boldsymbol{\Pi})\cdot\boldsymbol{u}}.\end{aligned} \tag{6.35}$$

When this is subtracted from (6.32), all these terms happily cancel with various bits that come out when we work out the divergence in the right-hand side of (6.32). Namely, keeping terms in the same order as they appeared originally in (6.32) and crossing out those that cancel with similar terms in (6.35),

$$\begin{aligned}\frac{\partial\langle E\rangle}{\partial t} = &-\cancel{\frac{mu^2}{2}\boldsymbol{\nabla}\cdot(n\boldsymbol{u})} - \cancel{mn\boldsymbol{u}\cdot\boldsymbol{\nabla}\frac{u^2}{2}} - \boldsymbol{\nabla}\cdot\left(\boldsymbol{u}\,\frac{3}{2}\,nk_\mathrm{B}T\right)\\ &- P\boldsymbol{\nabla}\cdot\boldsymbol{u} - \cancel{\boldsymbol{u}\cdot\boldsymbol{\nabla}P} - \cancel{(\boldsymbol{\nabla}\cdot\boldsymbol{\Pi})\cdot\boldsymbol{u}} - \Pi_{ij}\partial_i u_j - \boldsymbol{\nabla}\cdot\boldsymbol{J}.\end{aligned} \tag{6.36}$$

Therefore,

$$\begin{aligned}\frac{\partial}{\partial t}\frac{3}{2}\,nk_\mathrm{B}T &= \frac{\partial\langle E\rangle}{\partial t} - \frac{\partial}{\partial t}\frac{mnu^2}{2}\\ &= -\underbrace{\boldsymbol{\nabla}\cdot\left(\boldsymbol{u}\,\frac{3}{2}\,nk_\mathrm{B}T\right)}_{\substack{\text{internal-energy flux}\\ \text{due to mean flow}}} - \underbrace{P\boldsymbol{\nabla}\cdot\boldsymbol{u}}_{\substack{\text{compressional}\\ \text{heating}}} - \underbrace{\Pi_{ij}\partial_i u_j}_{\substack{\text{viscous}\\ \text{heating}}} - \underbrace{\boldsymbol{\nabla}\cdot\boldsymbol{J}}_{\text{heat flux}}.\end{aligned} \tag{6.37}$$

Our old energy-conservation equation (5.18) is recovered if we set $\boldsymbol{u} = 0$ and $n = \mathrm{const}$ (which is the assumption under which we derived it in §5.3.1), but we now know better and see that if we do retain the flow, a number of new terms appear, all with straightforward physical meaning (so our algebra is vindicated).

As was argued in §6.4.2 [see discussion around (6.25)], we cannot really assume $n = \mathrm{const}$ and so we need to use the continuity equation (6.17) to split off the rate of change of $n$ from the rate of change of $T$ in the left-hand side of (6.37). After unpacking also the first term on the right-hand side, this gives us a nice cancellation:

$$\frac{\partial}{\partial t}\frac{3}{2}\,nk_\mathrm{B}T = \frac{3}{2}\,nk_\mathrm{B}\frac{\partial T}{\partial t} + \cancel{\frac{3}{2}\,k_\mathrm{B}T\frac{\partial n}{\partial t}} = -\cancel{\frac{3}{2}\,k_\mathrm{B}T\boldsymbol{\nabla}\cdot(n\boldsymbol{u})} - \frac{3}{2}\,nk_\mathrm{B}\boldsymbol{u}\cdot\boldsymbol{\nabla}T + \text{the rest of terms}. \tag{6.38}$$

Hence, finally, we get the desired equation for the evolution of temperature:

$$\boxed{\frac{3}{2}nk_{\rm B}\left(\frac{\partial T}{\partial t}+\boldsymbol{u}\cdot\boldsymbol{\nabla}T\right)=-P\boldsymbol{\nabla}\cdot\boldsymbol{u}-\mathit{\Pi}_{ij}\partial_i u_j-\boldsymbol{\nabla}\cdot\boldsymbol{J}}. \tag{6.39}$$

This reduces to (5.18) if we set $T = T(z)$ and $\boldsymbol{u} = 0$:[30]

$$\frac{3}{2}nk_{\rm B}\frac{\partial T}{\partial t}=-\frac{\partial J_z}{\partial z}, \tag{6.40}$$

or, if we allow $\boldsymbol{u} = u_x(z)\hat{\boldsymbol{x}}$,

$$\frac{3}{2}nk_{\rm B}\frac{\partial T}{\partial t}=-\frac{\partial J_z}{\partial z}-\mathit{\Pi}_{zx}\frac{\partial u_x}{\partial z}, \tag{6.41}$$

capturing also viscous heating (in §6.7.2, we will see that the corresponding term is always positive, so viscous heating is indeed heating).

The temperature equation (6.39) was already found in Exercise 5.3 on general conservation grounds,[31] but now we have derived it kinetically and, as a result, we know precisely how to calculate $\mathit{\Pi}_{ij}$ [see (6.23)] and $\boldsymbol{J}$ [see (6.33)], provided that we can solve the kinetic equation (6.14) and obtain $\delta F$. In order to solve it, we must have an explicit expression for $C[F]$.

## 6.5. *Collision Operator*

For ideal gas, the explicit expression for collision operator (integral, quadratic in $F$, as per the discussion at the end of §6.3) was derived by Boltzmann (see, e.g., Boltzmann 1995; Chapman & Cowling 1991; Dellar 2015). I will not present this derivation here, but instead use the basic criteria that must be satisfied by the collision operator to come up with a very simple model for it (not quantitatively correct, but good enough for our purposes).

• First, the effect of collisions must be *to drive the particle distribution towards local thermodynamic equilibrium*, i.e., the local Maxwellian (5.10). Once this distribution is achieved, since the fast-time-scale effect of collisions is local to any given fluid element, the collisions should not change the local Maxwellian:

$$C[F_{\rm M}]=0. \tag{6.42}$$

---

If one derives the collision operator based on an explicit microphysical model of particle collisions, one can then *prove* that $C[F] = 0$ *implies* $F = F_{\rm M}$ and also that collisions always drive the distribution towards $F_{\rm M}$ (a simple example of such a calculation, involving deriving a collision operator from "first principles" of particle motion, can be found in §6.9). This property is associated with the so-called *Boltzmann's H-Theorem*, which is the law of entropy increase for kinetic systems. This belongs to a more advanced course of kinetic theory (e.g., Dellar 2015).

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• Secondly, *the relaxation to the local Maxwellian must occur on the collisional time scale* $\tau_{\rm c} = (\sigma n v_{\rm th})^{-1}$ [see (4.4)]. This depends on $n$ and $T$, so, in general, $\tau_{\rm c}$ is a function of $\boldsymbol{r}$. In a more quantitative theory, it transpires that it can also be a function of $\boldsymbol{v}$ (see discussion in §6.1.3).

[30] Strictly speaking, we must still allow very small flows needed to establish pressure balance; see discussion leading to (6.26).

[31] Note its interpretation suggested by the last part of that exercise: parcels of gas move around at velocity $\boldsymbol{u}$ behaving adiabatically except for heat fluxes and viscous heating.

• Thirdly, as I have already explained in §6.4, *elastic collisions must not change the total number, momentum or energy density of the particles* and so the collision operator satisfies the *conservation properties* (6.16), (6.19) and (6.31).

Arguably the simplest possible form of the collision operator that satisfies these criteria is the so-called *Krook operator* (also known as the *BGK operator*, after Bhatnagar–Gross–Krook):

$$\boxed{C[F] = -\frac{F - F_{\rm M}}{\tau_{\rm c}} = -\frac{1}{\tau_{\rm c}}\,\delta F}\,. \tag{6.43}$$

To satisfy the conservation laws (6.16), (6.19) and (6.31), we must have

$$\int \mathrm{d}^3\boldsymbol{v}\,\delta F = 0, \quad \int \mathrm{d}^3\boldsymbol{v}\,m\boldsymbol{v}\delta F = 0, \quad \int \mathrm{d}^3\boldsymbol{v}\,\frac{mv^2}{2}\,\delta F = 0. \tag{6.44}$$

These conditions are indeed satisfied because, as argued at the beginning of §6.4.3, we are, without loss of generality, committed to considering only such deviations from the local Maxwellian that contain no perturbation of $n$, $\boldsymbol{u}$ or energy.

The Krook operator is, of course, grossly simplified and inadequate for many kinetic calculations—and it certainly will not give us quantitatively precise values of transport coefficients. However, where it loses in precision it compensates in analytical simplicity and it is amply sufficient for demonstrating the basic idea of the calculation of these coefficients. The process of enlightened guesswork (also known as *modelling*) that we followed in devising it is also quite instructive as an illustration of how one comes up with a simple physically sensible model where the exact nature of the underlying process (in this case, collisions) might be unknown or too difficult to incorporate precisely, but it is clear what criteria must be respected by any sensible theory.

### 6.6. *Solution of the Kinetic Equation*

The kinetic equation (6.14) with the Krook collision operator (6.43) is

$$\frac{\partial F}{\partial t} + \boldsymbol{v}\cdot\boldsymbol{\nabla}F = -\frac{F - F_{\rm M}}{\tau_{\rm c}} = -\frac{1}{\tau_{\rm c}}\,\delta F. \tag{6.45}$$

Suppose that $\delta F \ll F_{\rm M}$ and also that the spatiotemporal variations of $\delta F$ occur on the same (large) scales as those of $F_{\rm M}$ (we will confirm in a moment that these are self-consistent assumptions). Then, in the left-hand side of (6.45), we can approximate $F \approx F_{\rm M}$. This instantly gives us an expression for the deviation from the Maxwellian:

$$\delta F \approx -\tau_{\rm c}\left(\frac{\partial F_{\rm M}}{\partial t} + \boldsymbol{v}\cdot\boldsymbol{\nabla}F_{\rm M}\right). \tag{6.46}$$

To avoid various minor, overcomeable, but tedious mathematical complications (of which we had enough in §6.4!), let us specialise to the 1D case[32] that I have used repeatedly to obtain simple answers: $F_{\rm M} = F_{\rm M}(z,\boldsymbol{v})$, $T = T(z)$, $\boldsymbol{u} = u_x(z)\hat{\boldsymbol{x}}$, although we now know that we must also assume $n = n(z)$ to ensure pressure balance (6.25). Then (6.46) becomes

$$\delta F \approx -\tau_{\rm c}\left(\frac{\partial F_{\rm M}}{\partial t} + v_z\frac{F_{\rm M}}{\partial z}\right), \tag{6.47}$$

[32] You will find the more general, 3D, version of this calculation in §6.8.

where $F_M$ is given by (6.11):[33]

$$F_{\rm M}(z,\boldsymbol{v}) = \frac{n(z)}{[2\pi k_{\rm B}T(z)/m]^{3/2}}\exp\left\{-\frac{m|\boldsymbol{v}-u_x(z)\hat{\boldsymbol{x}}|^2}{2k_{\rm B}T(z)}\right\}. \tag{6.48}$$

In the same approximation, we expect that all temporal evolution of $F_M$ (owing to the temporal evolution of $n$, $T$ and $u_x$) occurs on diffusive time scales, and so we can argue that, in (6.47), $\partial F_M/\partial t$ is negligible. Indeed, let us assess the magnitude of the two terms in (6.47):

$$\tau_{\rm c}v_z\frac{\partial F_{\rm M}}{\partial z} \sim \frac{\tau_{\rm c}v_{\rm th}}{l}F_{\rm M} \sim \frac{\lambda_{\rm mfp}}{l}F_{\rm M}, \tag{6.49}$$

$$\tau_{\rm c}\frac{\partial F_{\rm M}}{\partial t} \sim \frac{\tau_{\rm c}}{\tau_{\rm diff}}F_{\rm M} \sim \left(\frac{\lambda_{\rm mfp}}{l}\right)^2 F_{\rm M}, \tag{6.50}$$

where the latter estimate comes from anticipating the size of $\partial/\partial t$ as in §5.6.3. Thus, provided $l \gg \lambda_{\rm mfp}$, i.e., provided that all spatial variations of $F_M$ are macroscopic, we conclude that the $\partial F_M/\partial t$ term must be neglected entirely if we are expanding in the small parameter $\lambda_{\rm mfp}/l$. Note that (6.49) also confirms that $\delta F \ll F_M$, an assumption that we needed to write (6.46). You might object that, technically speaking, we do not yet know that, for macroscopic quantities, $\partial/\partial t \sim v_{\rm th}\lambda_{\rm mfp}\partial^2/\partial z^2 \sim 1/\tau_{\rm diff}$, but the idea here is to "order" the time derivative in this way and then confirm that the resulting approximate solution will satisfy this ordering. This may well be your first experience of this kind of skulduggery, but this is how serious things are done, and it is worth learning how to do them!

Thus, our solution (6.47) is now quite compact: differentiating the local Maxwellian (6.48),

$$\begin{aligned}\delta F &\approx -\tau_{\rm c}v_z\frac{\partial F_{\rm M}}{\partial z}\\ &= -\tau_{\rm c}v_z\left[\frac{1}{n}\frac{\partial n}{\partial z} - \frac{3}{2}\frac{1}{T}\frac{\partial T}{\partial z} + \frac{m|\boldsymbol{v}-u_x\hat{\boldsymbol{x}}|^2}{2k_{\rm B}T^2}\frac{\partial T}{\partial z} + \frac{m}{2k_{\rm B}T}2(\boldsymbol{v}-u_x\hat{\boldsymbol{x}})\cdot\hat{\boldsymbol{x}}\frac{\partial u_x}{\partial z}\right]F_{\rm M}.\end{aligned} \tag{6.51}$$

If we now rename $\boldsymbol{v}-u_x\hat{\boldsymbol{x}} = \boldsymbol{w}$, recall $2k_BT/m = v_{\rm th}$ and use (6.25) to set $(1/n)\partial n/\partial z = -(1/T)\partial T/\partial z$, we get, finally,

$$\boxed{\delta F = -\tau_{\rm c}w_z\left[\left(\frac{w^2}{v_{\rm th}^2}-\frac{5}{2}\right)\frac{1}{T}\frac{\partial T}{\partial z} + \frac{2w_x}{v_{\rm th}^2}\frac{\partial u_x}{\partial z}\right]F_{\rm M}}. \tag{6.52}$$

Thus, we have solved the kinetic equation and found the small deviation of the particle distribution function from the local Maxwellian caused by mean velocity and temperature gradients. The first line of (6.51) is perhaps the most transparent as to the mechanism of this deviation: $\delta F$ is simply the result of taking a local Maxwellian and letting it evolve ballistically for a time $\tau_c$, with all particles flying in straight lines at their initial velocities. Because $\tau_c$ is small, they only have an opportunity to do this for a short time before collisions restore local equilibrium, and so the local Maxwellian gets only slightly perturbed.

Note that $\delta F$ is *neither Maxwellian nor isotropic*—as indeed ought to be the case as it arises from the global equilibrium being broken by the presence of flows (which have a direction, in our case, $x$) and gradients (which also have a direction, in our case, $z$). The

[33] Assuming, as per (6.26), that the flows $u_z$ necessary to maintain pressure balance (6.25) are small.

deviation from the Maxwellian is small because the departures from the equilibrium—the gradients—are macroscopic (i.e., the corresponding time and spatial scales are long compared to collisional scales $\tau_c$ and $\lambda_{\rm mfp}$).

If our collision operator had been a more realistic and, therefore, much more complicated, integral operator than the Krook model one, solving the kinetic equation would have involved quite a lot of hard work inverting this operator—while with the Krook operator, that inversion was simply multiplication by $\tau_c$, which took us painlessly from (6.45) to (6.47). You will find the strategies for dealing with the true Boltzmann collision operator in Chapman & Cowling (1991) or Lifshitz & Pitaevskii (1981), and a simple example of inverting a differential collision operator in §6.9.5.

**Exercise 6.4.** Check that the solution (6.52) satisfies the particle, momentum and energy conservation conditions (6.44).

## 6.7. *Calculation of Fluxes*

Finally, we use the solution (6.52) in (6.24) and (6.34) to calculate the fluxes.

### 6.7.1. *Momentum Flux*

The momentum flux (6.24) is

$$\begin{aligned} \Pi_{zx} &= \int d^3\boldsymbol{w}\, m w_z w_x \delta F \\ &= -m\tau_c \int d^3\boldsymbol{w}\, w_z^2 w_x \left[\left(\frac{w^2}{v_{\rm th}^2} - \frac{5}{2}\right)\frac{1}{T}\frac{\partial T}{\partial z} + \frac{2w_x}{v_{\rm th}^2}\frac{\partial u_x}{\partial z}\right] F_{\rm M}(w) \\ &= -\left[\frac{2m\tau_c}{v_{\rm th}^2}\int d^3\boldsymbol{w}\, w_z^2 w_x^2 F_{\rm M}(w)\right]\frac{\partial u_x}{\partial z} \equiv -\eta\,\frac{\partial u_x}{\partial z}, \end{aligned} \tag{6.53}$$

where the term involving $\partial T/\partial z$ vanished because its integrand was odd in $w_x$. Satisfyingly, we have found that the momentum flux is proportional to the mean-velocity gradient, as I have previously argued it must be [see (5.40)]. The coefficient of proportionality between them is, by definition, the *dynamical viscosity*, the expression for which is, therefore,

$$\begin{aligned} \eta &= \frac{2m\tau_c}{v_{\rm th}^2}\int d^3\boldsymbol{w}\, w_z^2 w_x^2 F_{\rm M}(w) \\ &= \frac{2m\tau_c}{v_{\rm th}^2} \underbrace{\int_0^\infty dw\, w^6 \frac{n}{(\sqrt{\pi}v_{\rm th})^3} e^{-w^2/v_{\rm th}^2}}_{=15nv_{\rm th}^4/16\pi} \underbrace{\int_0^\pi d\theta\, \sin^3\theta\cos^2\theta}_{=4/15} \underbrace{\int_0^{2\pi} d\phi\, \cos^2\phi}_{=\pi} \\ &= \frac{1}{2}\, m n v_{\rm th}^2 \tau_c = \frac{1}{2}\, m n \lambda_{\rm mfp} v_{\rm th}. \end{aligned} \tag{6.54}$$

No surprises here: the same dependence on $\lambda_{\rm mfp}$ and temperature (via $v_{\rm th}$) as in (6.4), but a different numerical coefficient.[34] This coefficient depends on the form of the collision operator and so, since the collision operator that we used is only a crude model, the coefficient is order-unity wrong. It is progress, however, that we now know what to do

[34]Note that the angle dependence of the integrand in (6.3) that we so proudly worked out in §6.1 was in fact wrong. However, the derivation in §6.1, while "dodgy," was not useless: it highlighted much better than the present, more systematic, one that momentum and energy are transported because of particles wandering between regions of gas with different $u_x$ and $T$.

to calculate viscosity precisely for any given model of collisions. You will find many such precise calculations in, e.g., Chapman & Cowling (1991).

6.7.2. *Heat Flux*

A similar calculation of the velocity integral in (6.34) gives us the heat flux:

$$\begin{aligned} J_z &= \int \mathrm{d}^3\boldsymbol{w}\, \frac{mw^2}{2}\, w_z \delta F \\ &= -\frac{m\tau_c}{2} \int \mathrm{d}^3\boldsymbol{w}\, w_z^2 w^2 \left[\left(\frac{w^2}{v_{\mathrm{th}}^2} - \frac{5}{2}\right)\frac{1}{T}\frac{\partial T}{\partial z} + \frac{2w_x}{v_{\mathrm{th}}^2}\frac{\partial u_x}{\partial z}\right] F_{\mathrm{M}}(w) \\ &= -\left[\frac{m\tau_c}{2T}\int \mathrm{d}^3\boldsymbol{w}\, w_z^2 w^2 \left(\frac{w^2}{v_{\mathrm{th}}^2} - \frac{5}{2}\right) F_{\mathrm{M}}(w)\right]\frac{\partial T}{\partial z} \equiv -\varkappa \frac{\partial T}{\partial z}, \end{aligned} \tag{6.55}$$

where the term involving $\partial u_x/\partial z$ vanished because its integrand was odd in $w_x$. The heat flux turns out to be proportional to the temperature gradient, as expected [see (5.39)]. The expression for the *thermal conductivity* is, therefore,

$$\begin{aligned} \varkappa &= \frac{m\tau_c}{2T}\int \mathrm{d}^3\boldsymbol{w}\, w_z^2 w^2 \left(\frac{w^2}{v_{\mathrm{th}}^2} - \frac{5}{2}\right) F_{\mathrm{M}}(w) \\ &= \frac{k_{\mathrm{B}}\tau_c}{v_{\mathrm{th}}^2} \underbrace{\int_0^\infty \mathrm{d}w\, w^6 \left(\frac{w^2}{v_{\mathrm{th}}^2} - \frac{5}{2}\right) \frac{n}{(\sqrt{\pi}v_{\mathrm{th}})^3}\, e^{-w^2/v_{\mathrm{th}}^2}}_{=15nv_{\mathrm{th}}^4/16\pi} \underbrace{\int_0^\pi \mathrm{d}\theta\, \sin\theta\cos^2\theta}_{=2/3} \underbrace{\int_0^{2\pi}\mathrm{d}\phi}_{=2\pi} \\ &= \frac{5}{4}nk_{\mathrm{B}}v_{\mathrm{th}}^2\tau_c = \frac{5}{6}nc_1\lambda_{\mathrm{mfp}}v_{\mathrm{th}}, \quad c_1 = \frac{3}{2}k_{\mathrm{B}}. \end{aligned} \tag{6.56}$$

Again, we have the same kind of expression as in (6.7), but with a different prefactor. You now have enough experience to spot that these prefactors come from the averaging of various angle and speed dependences over the underlying Maxwellian distribution—and the prefactors are nontrivial basically because of intrinsic correlations between, e.g., in this case, particle energy, the speed and angle at which it moves (transport), and the form of the non-Maxwellian correction to the local equilibrium which is caused by the temperature gradient and enables heat to flow on average.

Since we now have the heat equation (6.41) including also viscous heating, it is worth writing out its final form: using (6.56) and (6.53), we get

$$\frac{3}{2}nk_{\mathrm{B}}\frac{\partial T}{\partial t} = \varkappa\frac{\partial^2 T}{\partial z^2} + \eta\left(\frac{\partial u_x}{\partial z}\right)^2. \tag{6.57}$$

The viscous term is manifestly positive, so does indeed represent heating.

In terms of diffusivities, $D_T = 2\varkappa/3nk_{\mathrm{B}}$ [see (5.50)] and $\nu = \eta/mn$ [see (5.51)],

$$\boxed{\frac{\partial T}{\partial t} = D_T\frac{\partial^2 T}{\partial z^2} + \frac{2m}{3k_{\mathrm{B}}}\nu\left(\frac{\partial u_x}{\partial z}\right)^2}. \tag{6.58}$$

This equation and the momentum equation (6.22) combined with (6.53),

$$\boxed{\frac{\partial u_x}{\partial t} = \nu\frac{\partial^2 u_x}{\partial z^2}}, \tag{6.59}$$

form a closed system, completely describing the evolution of the gas.

**Exercise 6.5. Fick's Law of Diffusion.** (a) Starting from the kinetic equation for the distribution function $F^*(t,z,\boldsymbol{v})$ of some labelled particle admixture in a gas, derive the diffusion equation

$$\frac{\partial n^*}{\partial t} = D\frac{\partial^2 n^*}{\partial z^2} \tag{6.60}$$

for the number density $n^*(t,z) = \int \mathrm{d}^3\boldsymbol{v}\, F^*(t,z,\boldsymbol{v})$ of the labelled particles (assuming $n^*$ changes only in the $z$ direction). Derive also the expression for the diffusion coefficient $D$, given
—the molecular mass $m^*$ of the labelled particles,
—the temperature $T$ of the ambient gas (assume $T$ is uniform),
—collision frequency $\nu_\mathrm{c}^*$ of the labelled particles with the ambient ones.
Assume that the ambient gas is static (no mean flows), that the density of the labelled particles is so low that they only collide with the unlabelled particles (and not each other) and that the frequency of these collisions is much larger than the rate of change of any mean quantities. Use the Krook collision operator, assuming that collisions relax the distribution of the labelled particles to a Maxwellian $F_\mathrm{M}^*$ with density $n^*$ and the same velocity (zero) and temperature ($T$) as the ambient unlabelled gas. *Hint.* Is the momentum of the labelled particles conserved by collisions? You should discover that self-diffusion is related to the mean velocity $u_z^*$ of the labelled particles (you can assume $u_z^* \ll v_\mathrm{th}$). You can calculate this velocity either directly from $\delta F^* = F^* - F_\mathrm{M}^*$ or from the momentum equation for the labelled particles.

(b) Derive the momentum equation for the mean flow $u_z^*$ of the labelled particles and obtain the result you have known since school: that the friction force (the collisional drag exerted on labelled particles by the ambient population) is proportional to the mean velocity of the labelled particles. What is the proportionality coefficient (the "drag coefficient")? This, by the way, is the "Aristotelian equation of motion"—Aristotle thought force was generally proportional to velocity. It took a while for another brilliant man to figure out the more general formula.

Show from the momentum equation that you have derived that the flux of the labelled particles is proportional to their pressure gradient:

$$\varPhi_z^* = n^* u_z^* = -\frac{1}{m^*\nu_\mathrm{c}^*}\frac{\partial P^*}{\partial z}. \tag{6.61}$$

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## 6.8. *Calculation of Fluxes in 3D*

For completeness, here is a more general calculation of the fluxes, for the case of arbitrary 3D spatially dependent density, temperature, and mean flow velocity. While this is notionally a more involved derivation, some of you might in fact find it more appealing as it reveals the fundamental structure of the theory much more vividly.

Let us go back to the 3D solution (6.46) of the kinetic equation and consider now a 3D-inhomogeneous local Maxwellian

$$F_\mathrm{M}(\boldsymbol{r},\boldsymbol{v}) = \frac{n}{(\sqrt{\pi}\,v_\mathrm{th})^2}\,e^{-w^2/v_\mathrm{th}^2} = \frac{n(\boldsymbol{r})}{[2\pi k_\mathrm{B}T(\boldsymbol{r})/m]^{3/2}}\exp\left\{-\frac{m|\boldsymbol{v}-\boldsymbol{u}(\boldsymbol{r})|^2}{2k_\mathrm{B}T(\boldsymbol{r})}\right\}. \tag{6.62}$$

Then

$$\delta F = -\tau_\mathrm{c}\left(\frac{\partial \ln F_\mathrm{M}}{\partial t} + \boldsymbol{v}\cdot\boldsymbol{\nabla}\ln F_\mathrm{M}\right)F_\mathrm{M}. \tag{6.63}$$

Differentiate the Maxwellian:

$$\boldsymbol{\nabla}\ln F_\mathrm{M} = \frac{\boldsymbol{\nabla} n}{n} + \left(\frac{w^2}{v_\mathrm{th}^2} - \frac{3}{2}\right)\frac{\boldsymbol{\nabla} T}{T} + 2\,\frac{(\boldsymbol{\nabla}\boldsymbol{u})\cdot\boldsymbol{w}}{v_\mathrm{th}^2}, \tag{6.64}$$

$$\frac{\partial \ln F_\mathrm{M}}{\partial t} = \frac{1}{n}\frac{\partial n}{\partial t} + \left(\frac{w^2}{v_\mathrm{th}^2} - \frac{3}{2}\right)\frac{1}{T}\frac{\partial T}{\partial t} + 2\,\frac{\boldsymbol{w}}{v_\mathrm{th}^2}\cdot\frac{\partial \boldsymbol{u}}{\partial t}. \tag{6.65}$$

To calculate the time derivatives of the fluid quantities in the last equation, we will use the fluid equations (6.17), (6.39) and (6.21). To simplify algebra, we note that, by Galilean invariance, the values of heat conductivity and dynamical viscosity that we will end up computing cannot depend on the reference frame and so we may calculate them at a point where $\boldsymbol{u} = 0$ (or can be made so by a suitable Galilean transformation). Obviously, we must still retain all derivatives of $\boldsymbol{u}$.

**Exercise 6.6.** Repeat the calculation that follows without employing this ruse and convince yourself that the same result obtains.

Using $P = nk_{\rm B}T$ where opportune, (6.17), (6.39) and (6.21) then give us

$$\frac{1}{n}\frac{\partial n}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{u}, \tag{6.66}$$

$$\frac{1}{T}\frac{\partial T}{\partial t} = -\frac{2}{3}\left(\boldsymbol{\nabla}\cdot\boldsymbol{u} + \cancel{\frac{\Pi_{ij}\partial_i u_j}{nk_{\rm B}T}} + \cancel{\frac{\boldsymbol{\nabla}\cdot\boldsymbol{J}}{nk_{\rm B}T}}\right), \tag{6.67}$$

$$2\,\frac{\boldsymbol{w}}{v_{\rm th}^2}\cdot\frac{\partial\boldsymbol{u}}{\partial t} = -\boldsymbol{w}\cdot\left(\frac{\boldsymbol{\nabla}P}{P} + \cancel{\frac{\boldsymbol{\nabla}\cdot\boldsymbol{\Pi}}{P}}\right). \tag{6.68}$$

The terms that are crossed out are negligible in comparison with the ones that are retained (this can be ascertained *a posteriori*, once $\boldsymbol{J}$ and $\boldsymbol{\Pi}$ are known). Assembling the rest according to (6.65), we have

$$\frac{\partial\ln F_{\rm M}}{\partial t} = -\frac{2}{3}\frac{w^2}{v_{\rm th}^2}\boldsymbol{\nabla}\cdot\boldsymbol{u} - \boldsymbol{w}\cdot\left(\frac{\boldsymbol{\nabla}n}{n} + \frac{\boldsymbol{\nabla}T}{T}\right). \tag{6.69}$$

Finally, substituting (6.64) and (6.69) into (6.63), we arrive at

$$\delta F = -\tau_{\rm c}\left[\left(\frac{w^2}{v_{\rm th}^2} - \frac{5}{2}\right)\frac{\boldsymbol{w}\cdot\boldsymbol{\nabla}T}{T} + 2\,\frac{w_k w_l}{v_{\rm th}^2}\left(\partial_k u_l - \frac{1}{3}\,\delta_{kl}\boldsymbol{\nabla}\cdot\boldsymbol{u}\right)\right]F_{\rm M} \tag{6.70}$$

(where $\boldsymbol{v}$ has been replaced by $\boldsymbol{w}$ where necessary because we are at a point where $\boldsymbol{u} = 0$).

**Exercise 6.7.** Check that this $\delta F$ contains no density, momentum or energy perturbation.

Now we are ready to calculate the fluxes, according to (6.23) and (6.33). Similarly to what happened in §§6.7.1 and 6.7.2, the part of $\delta F$ containing $\boldsymbol{\nabla}T$ only contributes to the heat flux because it is odd in $\boldsymbol{w}$ and the part containing $\partial_k u_l$ only contributes to the momentum flux because it is even in $\boldsymbol{w}$.

The heat flux is the easier calculation:

$$\boldsymbol{J} = \int d^3\boldsymbol{w}\,\frac{mw^2}{2}\,\boldsymbol{w}\,\delta F = -\frac{m\tau_{\rm c}}{2T}\left[\int d^3\boldsymbol{w}\,\boldsymbol{w}\boldsymbol{w}\,w^2\left(\frac{w^2}{v_{\rm th}^2} - \frac{5}{2}\right)F_{\rm M}(w)\right]\cdot\boldsymbol{\nabla}T. \tag{6.71}$$

Since the angle average is $\langle w_i w_j\rangle = w^2\delta_{ij}/3$ (recall Exercise 1.3b), this becomes

$$\boldsymbol{J} = -\frac{mn\tau_{\rm c}}{2T}\underbrace{\left[\frac{4\pi}{3}\int_0^\infty dw\,w^6\left(\frac{w^2}{v_{\rm th}^2} - \frac{5}{2}\right)\frac{e^{-w^2/v_{\rm th}^2}}{(\sqrt{\pi}\,v_{\rm th})^3}\right]}_{=(5/4)v_{\rm th}^4}\boldsymbol{\nabla}T = -\varkappa\boldsymbol{\nabla}T, \tag{6.72}$$

where $\varkappa = (5/4)nk_{\rm B}v_{\rm th}^2\tau_{\rm c}$, in gratifying agreement with (6.56).

The momentum flux is a little more work because it is a matrix:

$$\Pi_{ij} = \int d^3\boldsymbol{w}\,mw_iw_j\delta F = -\frac{2m\tau_{\rm c}}{v_{\rm th}^2}\left[\int d^3\boldsymbol{w}\,w_iw_jw_kw_lF_{\rm M}(w)\right]\left(\partial_k u_l - \frac{1}{3}\,\delta_{kl}\boldsymbol{\nabla}\cdot\boldsymbol{u}\right). \tag{6.73}$$

The angle average is $\langle w_iw_jw_kw_l\rangle = w^4(\delta_{ij}\delta_{kl} + \delta_{ik}\delta jl + \delta_{il}\delta_{jk})/15$ (Exercise 1.3c). Therefore,

$$\Pi_{ij} = -\frac{2mn\tau_{\rm c}}{v_{\rm th}^2}\underbrace{\left[\frac{4\pi}{15}\int_0^\infty dw\,w^6\,\frac{e^{-w^2/v_{\rm th}^2}}{(\sqrt{\pi}\,v_{\rm th})^3}\right]}_{=v_{\rm th}^4/4}\left(\partial_i u_j + \partial_j u_i - \frac{2}{3}\,\delta_{ij}\boldsymbol{\nabla}\cdot\boldsymbol{u}\right)$$

$$= -\eta\left(\partial_i u_j + \partial_j u_i - \frac{2}{3}\,\delta_{ij}\boldsymbol{\nabla}\cdot\boldsymbol{u}\right), \tag{6.74}$$

where $\eta = mnv_{\rm th}^2\tau_{\rm c}/2$, the same as found in (6.54). Besides the expression for the dynamical viscosity, we have now also worked out the tensor structure of the viscous stress, as promised earlier [after (5.42)].

## 6.9. *Kinetic Theory of Brownian Particles*

This section is for the keen, the curious and the impatient (impatient for material for which they otherwise might have to wait another year, at least).

Here I will construct the kinetic theory for a particular model of a gas, which will help bring together some of the ideas that appeared above, in particular in §§5.7 and 6. Thus, this section serves as an example of a simple application of all the theoretical machinery that we have constructed.

### 6.9.1. *Langevin Equation*

A very famous and simple way of modelling the behaviour of a particle in a gas is the *Langevin equation:* in 1D (for simplicity), the velocity of a particle is declared to satisfy

$$\boxed{\dot{v} + \nu v = \chi(t)}\,. \tag{6.75}$$

Here $\nu$ is some effective damping rate representing the slowing down of our particle due to friction with the particles of the ambient gas and $\chi(t)$ is a random force representing the random kicks that our particle receives from them. This is a good model not for a gas molecule but for some macroscopic alien particle moving about in the gas—e.g., a particle of pollen in air. It is called a *Brownian particle* and its motion *Brownian motion* after the pioneering researcher who discovered it.

The frictional force proportional to velocity is simply the Stokes drag on a body moving through a viscous medium. The force $\chi(t)$ is postulated to be a Gaussian random process with zero average, $\langle\chi(t)\rangle = 0$, and zero correlation time (*Gaussian white noise*), i.e., its time correlation function is taken to be

$$\langle\chi(t)\chi(t')\rangle = A\delta(t-t'), \tag{6.76}$$

where $A$ is some (known) constant. We can relate this constant and the drag rate $\nu$ to the temperature of the ambient gas (with which we shall assume the Brownian particles to be in thermal equilibrium) by noticing that (6.75) implies, after multiplication by $v$ and averaging,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\frac{\langle v^2\rangle}{2} + \nu\langle v^2\rangle = \langle v(t)\chi(t)\rangle &= \left\langle\left\{v(0) + \int_0^t \mathrm{d}t'\left[-\nu v(t') + \chi(t')\right]\right\}\chi(t)\right\rangle \\ &= \cancel{\langle v(0)\chi(t)\rangle} + \int_0^t \mathrm{d}t'\left[-\nu\cancel{\langle v(t')\chi(t)\rangle} + \langle\chi(t')\chi(t)\rangle\right] = \frac{A}{2}.\end{aligned} \tag{6.77}$$

Here the two terms that vanished did so because they are correlations between the force at time $t$ and the velocity at an earlier time—so the latter cannot depend on the former, the average of the product is the product of averages and we use $\langle\chi(t)\rangle = 0$. The only term that did not vanish was calculated using (6.76) (the factor of 1/2 appeared because the integration was up to $t$: only half of the delta function). In the statistical steady state (equilibrium), $\mathrm{d}\langle v^2\rangle/\mathrm{d}t = 0$, so (6.77) gives us

$$\boxed{\langle v^2\rangle = \frac{A}{2\nu} = \frac{k_\mathrm{B}T}{m}}\,. \tag{6.78}$$

The last equality is inferred from the fact that, statistically, in 1D, $m\langle v^2\rangle = k_\mathrm{B}T$, where $T$ is the temperature of the gas and $m$ the mass of the particle [see (2.22)]. Thus, we will henceforth write

$$A = \nu\frac{2k_\mathrm{B}T}{m} = \nu v_\mathrm{th}^2. \tag{6.79}$$

### 6.9.2. *Diffusion in Velocity Space*

Let us now imagine a large collection of (non-interacting) Brownian particles, each of which satisfies (6.75) with, in general, a different realisation of the random force $\chi(t)$ and a different initial condition $v(0)$. The averages $\langle\ldots\rangle$ are averages over both $\chi(t)$ and $v(0)$. Let us work out the pdf of $v$, i.e., the probability density function for a particle to have velocity $v$ at time $t$. It is

$$f(t,v) = \langle \delta(v - v(t)) \rangle. \tag{6.80}$$

Here $v$ is the *value* of velocity in the probability of whose occurrence we are interested and $v(t)$ is the *actual random velocity* of the particle, over which the averaging is done. Indeed,

$$\langle \delta(v - v(t)) \rangle = \int \mathrm{d}v(t) \delta(v - v(t)) f(t, v(t)) = f(t,v), \quad \text{q.e.d.} \tag{6.81}$$

We shall now derive the evolution equation for $f$. First, the unaveraged delta function satisfies, formally,

$$\begin{aligned} \frac{\partial}{\partial t}\delta(v - v(t)) &= -\delta'(v - v(t))\dot{v}(t) \\ &= -\frac{\partial}{\partial v}\delta(v - v(t))\dot{v}(t) \\ &= -\frac{\partial}{\partial v}\delta(v - v(t))\left[-\nu v(t) + \chi(t)\right] \\ &= \frac{\partial}{\partial v}\left[\nu v - \chi(t)\right]\delta(v - v(t)). \end{aligned} \tag{6.82}$$

Averaging this and using (6.80), we get

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial v}\left[\nu v f - \langle \chi(t)\delta(v - v(t))\rangle\right]. \tag{6.83}$$

To find the average in the second term, we formally integrate (6.82):

$$\begin{aligned} \langle \chi(t)\delta(v - v(t))\rangle &= \left\langle \chi(t)\left\{\delta(v - v(0)) + \int_0^t \mathrm{d}t' \frac{\partial}{\partial v}\left[\nu v - \chi(t')\right]\delta(v - v(t'))\right\}\right\rangle \\ &= -\frac{\nu v_{\mathrm{th}}^2}{2}\frac{\partial}{\partial v} f(t,v). \end{aligned} \tag{6.84}$$

To obtain this result, we took $\delta(v - v(t'))$ to be independent of either $\chi(t)$ or $\chi(t')$, again by the causality principle: $v(t')$ can only depend on the force at times previous to $t'$. As a result of this, the first two terms vanished because $\langle \chi(t)\rangle = 0$ and in the last term we used Eqs. (6.76) and (6.79) and did the integral similarly to (6.77).

Finally, substituting (6.84) into (6.83), we get

$$\boxed{\frac{\partial f}{\partial t} = \nu \frac{\partial}{\partial v}\left(v f + \frac{v_{\mathrm{th}}^2}{2}\frac{\partial f}{\partial v}\right)}. \tag{6.85}$$

This is very obviously a diffusion equation in velocity space, with an additional drag (the $vf$ term). The steady-state ($\partial f/\partial t = 0$) solution of (6.85) that normalises to unity is

$$f = \frac{1}{\sqrt{\pi}\, v_{\mathrm{th}}}\, e^{-v^2/v_{\mathrm{th}}^2}, \tag{6.86}$$

a 1D Maxwellian, as it ought to be, in equilibrium.

It is at this point that we should be struck by the realisation that what we have just derived is the collision operator for Brownian particles. In this simple model, it is the differential operator in the right-hand side of (6.85). As a collision operator must do, it pushes the particle distribution towards a Maxwellian—since we derived the collision operator from "first principles" of particle motion, we are actually able to conclude that the equilibrium distribution is Maxwellian simply by solving (6.85) in steady state (rather than having to bring the Maxwellian in as a requirement for constructing a model of collisions, as we did in §6.5).

There is one important difference between the collision operator in (6.85) and the kind of collision operator, discussed in §6.5, that would be suitable for gas molecules: whereas the Brownian particles' collision operator does conserve both their number and their energy, it certainly does not conserve momentum (**Exercise**: check these statements). This is not an error: since the Brownian particles experience a drag force from the ambient gas, it is not surprising that they should lose momentum as a result (cf. Exercise 6.5).

Clearly, (6.85) is the kinetic equation for Brownian particles. Where then, might you ask, is then the spatial dependence of this distribution—i.e., where is the $\boldsymbol{v}\cdot\boldsymbol{\nabla}F$ term that appears in our prototypical kinetic equation (6.14)? This will be recovered in §6.9.4.

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**Exercise 6.8. Particle Heating.** What happens to our particles if $\nu = 0$ and $A$ is fixed to some constant? Explain the following statement: the drag on the particles limits how much their distribution can be heated.

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### 6.9.3. *Brownian Motion*

Let us now preoccupy ourselves with the question of how Brownian particles move in space. The displacement of an individual particle from its initial position is

$$z(t) = \int_0^t \mathrm{d}t' v(t'), \tag{6.87}$$

and so the mean square displacement is

$$\langle z^2(t)\rangle = \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \langle v(t')v(t'')\rangle. \tag{6.88}$$

Thus, in order to calculate $\langle z^2\rangle$, we need to know the *time-correlation function* $\langle v(t')v(t'')\rangle$ of the particle velocities.

This is easy to work out because we can solve (6.75) explicitly:

$$v(t) = v(0)e^{-\nu t} + \int_0^t \mathrm{d}\tau \chi(\tau) e^{-\nu(t-\tau)}. \tag{6.89}$$

This says that the "memory" of the initial condition decays exponentially and so, for $\nu t \gg 1$, we can simply omit the first term (or formally consider our particle to have started from rest at $t = 0$). The mean square displacement (6.88) becomes in this long-time limit

$$\langle z^2(t)\rangle = \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \int_0^{t'} \mathrm{d}\tau' \int_0^{t''} \mathrm{d}\tau'' \langle \chi(\tau')\chi(\tau'')\rangle e^{-\nu(t'-\tau'+t''-\tau'')} = \frac{v_{\mathrm{th}}^2}{\nu}\, t, \tag{6.90}$$

where we have again used (6.76) and (6.79) and integrated the exponentials, carefully paying attention to the integration limits, to what happens when $t' > t''$ vs. $t' < t''$, and finally retaining only the largest term in the limit $\nu t \gg 1$.

Thus, the mean square displacement of our particle is proportional to time. It might be illuminating at this point for you to compare this particular model of diffusion with the model discussed in §5.7.2 and think about why the two are similar.

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**Exercise 6.9.** Calculate $\langle v(t')v(t'')\rangle$ carefully and show that the correlation time of the particle velocity is $1/\nu$ (i.e., argue that this is the typical time over which the particles "remembers" its history).

**Exercise 6.10.** Work out $\langle z^2(t)\rangle$ without assuming $\nu t \gg 1$ and find what it is when $\nu t \ll 1$? Does this answer make physical sense?

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### 6.9.4. *Kinetic Equation for Brownian Particles*

Now let us determine the joint distribution of particle velocities and positions, i.e., the full pdf of the particles in the phase space: similarly to (6.80), we have

$$F(t, z, v) = N\langle \delta(z - z(t))\delta(v - v(t))\rangle, \tag{6.91}$$

where $v(t)$ continues to satisfy (6.75) and $z(t)$ satisfies

$$\dot{z} = v(t). \tag{6.92}$$

The factor of $N$, the number of particles, has been introduced to make $F$ consistent with our convention that it should be normalised to $N$, rather than to unity [see (5.1)].

The derivation of the evolution equation for $F$ is analogous to the derivation in §6.9.2:

$$\begin{aligned}\frac{\partial F}{\partial t} &= -N\langle\delta'(z-z(t))\dot{z}(t)\delta(v-v(t))+\delta(z-z(t))\delta'(v-v(t))\dot{v}(t)\rangle\\ &= -N\left\langle\left[\frac{\partial}{\partial z}\dot{z}(t)+\frac{\partial}{\partial v}\dot{v}(t)\right][\delta(z-z(t))\delta(v-v(t))]\right\rangle\\ &= -N\left\langle\left[\frac{\partial}{\partial z}v+\frac{\partial}{\partial v}(-\nu v+\chi)\right][\delta(z-z(t))\delta(v-v(t))]\right\rangle\\ &= -v\,\frac{\partial F}{\partial z}+\frac{\partial}{\partial v}\left[\nu vF-N\langle\chi(t)\delta(z-z(t))\delta(v-v(t))\rangle\right] \end{aligned} \tag{6.93}$$

and, with the average involving $\chi$ again calculated by formally integrating the unaveraged version of the above equation for $\delta(z-z(t))\delta(v-v(t))$ and using causality to split correlations, we get, finally,

$$\boxed{\frac{\partial F}{\partial t}+v\,\frac{\partial F}{\partial z}=\nu\frac{\partial}{\partial v}\left(vF+\frac{v_{\rm th}^2}{2}\frac{\partial F}{\partial v}\right)\equiv C[F]}\,. \tag{6.94}$$

This is the kinetic equation for Brownian particles, analogous to (6.14), with the collision operator that we already derived in §6.9.2. Of course, (6.85) is just (6.94) integrated over all particle positions $z$.

### 6.9.5. *Diffusion in Position Space*

The collision operator in (6.94) is still pushing our pdf towards a Maxwellian, but it is, in general, only a local Maxwellian, with particle number density that can depend on $t$ and $z$:

$$F_{\rm M}(t,z,v)=\frac{n(t,z)}{\sqrt{\pi}\,v_{\rm th}}\,e^{-v^2/v_{\rm th}^2}. \tag{6.95}$$

This is the Brownian-gas analog of the local Maxwellian (5.10). Note that we are assuming that the temperature of the ambient gas is spatially homogeneous and constant in time, i.e., that $v_{\rm th}=$ const. Clearly, the pdf (6.95) represents the local equilibrium that will be achieved provided the right-hand side of (6.94) is dominant, i.e., provided that $n(t,z)$ changes sufficiently slowly in time compared to the collision rate $\nu$ and has a sufficiently long gradient scale length compared to $v_{\rm th}/\nu$ (the mean free path of Brownian particles).

We may now complete the kinetic theory of Brownian particles by deriving the evolution equation for their density $n(t,z)$. Let us do the same thing as we did in §6.4.1 and obtain this equation by integrating the kinetic equation (6.94) over all velocities. Expectedly, we get a continuity equation:

$$\frac{\partial n}{\partial t}+\frac{\partial}{\partial z}nu=0, \tag{6.96}$$

where $nu(t,z)=\int {\rm d}v\,vF(t,z,v)$ is the *particle flux*. Since the equilibrium solution (6.95) has no mean flow in it, all of the particle flux must be due to the (small) deviation of $F$ from $F_{\rm M}$, just like the momentum and heat fluxes in §6.2 arose due to such a deviation.

We shall solve for $\delta F=F-F_{\rm M}$ using the same method as in §6.6: Assuming $\delta F\ll F_{\rm M}$ and $\nu\gg v\partial/\partial z\gg\partial/\partial t$, we conclude from (6.94) that $\delta F$ must satisfy, approximately:

$$\frac{\partial}{\partial v}\left(v\delta F+\frac{v_{\rm th}^2}{2}\frac{\partial\delta F}{\partial v}\right)=\frac{v}{\nu}\frac{\partial F_{\rm M}}{\partial z}=\frac{v}{\nu n}\frac{\partial n}{\partial z}F_{\rm M}. \tag{6.97}$$

Inverting the collision operator, which is now a differential one, is a less trivial operation than with the Krook operator in §6.6, but only slightly less: noticing that $vF_{\rm M}=-(v_{\rm th}^2/2)\partial F_{\rm M}/\partial v$, we may integrate (6.97) once, reducing it to a first-order ODE:

$$\frac{\partial\delta F}{\partial v}+\frac{2v}{v_{\rm th}^2}\,\delta F=-\frac{1}{\nu n}\frac{\partial n}{\partial z}F_{\rm M}. \tag{6.98}$$

The solution of this is

$$\delta F=-\frac{v}{\nu n}\frac{\partial n}{\partial z}F_{\rm M}. \tag{6.99}$$

The integration constants are what they are because $\delta F$ must vanish at $v\to\pm\infty$ and because we require the density $n$ of the Maxwellian (6.95) to be the exact density, i.e., $\int \mathrm{d}v\,\delta F = 0$ (the logic of this was explained at the beginning of §6.4.3).

Finally, the particle flux is

$$nu = \int \mathrm{d}v\, v\delta F = -\frac{v_{\mathrm{th}}^2}{2\nu}\frac{\partial n}{\partial z} \tag{6.100}$$

and (6.96) becomes the diffusion equation for Brownian particles:

$$\boxed{\frac{\partial n}{\partial t} = D\,\frac{\partial^2 n}{\partial z^2}, \quad D = \frac{v_{\mathrm{th}}^2}{2\nu}}\,. \tag{6.101}$$

This is nothing but Fick's Law of Diffusion, which already made an appearance in §5.7 and in Exercises 6.2 and 6.5 and which we have now formally derived for Brownian particles.

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**Exercise 6.11.** Work out the kinetic theory of Brownian particles in 3D by generalising the above calculations to vector velocities $\boldsymbol{v}$ and positions $\boldsymbol{r}$. You may assume the vector components of the random force $\boldsymbol{\chi}(t)$ to be uncorrelated with each other, $\langle \chi_i(t)\chi_j(t')\rangle = A\delta_{ij}\delta(t-t')$.

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PART III

# Foundations of Statistical Mechanics

## 7. From Microphysics to Macrophysics

### 7.1. *What Are We Trying to Do?*

Thermodynamics was all about flows of energy, which we formalised in two ways:

$$\mathrm{d}U = \underbrace{\delta Q}_{\text{heat}} - \underbrace{\delta W}_{\text{work}} = T\mathrm{d}S - P\mathrm{d}V. \tag{7.1}$$

Note that $T$ and $S$ were *introduced* via their relationship with heat in reversible processes. All this was completely general. But to calculate anything specific, we needed two further pieces of information:

1) equation of state $P = P(T, V)$, e.g., $PV = Nk_{\mathrm{B}}T$ for ideal gas,

2) energy $U = U(T, V)$, e.g., $U = \frac{3}{2}Nk_{\mathrm{B}}T$ for monatomic ideal gas.

It was also useful to be able to calculate $S(T, V)$ and various other functions of state, but all that could be obtained from thermodynamics once the two ingredients above were in place.

Working these out always required some microphysical model of the substance that the system was made of (e.g., classical ideal gas). Similarly, for non-$PV$ systems, we always had some model (or engineering-style parametrisation) of the stuff that they were made of in order to determine, e.g., the tension $f(T, L)$ as a function of length $L$ and temperature $T$, the magnetisation $\boldsymbol{M}(T, \boldsymbol{B})$ as a function of magnetic field $\boldsymbol{B}$ and temperature $T$, etc. (there is always $T$ because there is always energy—a special quantity in Statistical Physics).

So, the goal is, *given a system with certain known microphysical properties (exactly what needs to be known, we will see shortly), to learn how to construct its equation of state and the relationship between its energy and temperature (as well as other parameters, e.g., $V$).*

To work out a specific algorithm for the construction of the thermodynamics of any given system, recall that the *free energy* satisfies

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V \tag{7.2}$$

and so, if we know $F(T, V)$, we can calculate everything particularly straightforwardly:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad \text{equation of state}, \tag{7.3}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad \text{entropy}, \tag{7.4}$$

$$U = F + TS, \quad \text{energy}, \tag{7.5}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \quad \text{heat capacity, etc.} \tag{7.6}$$

Thus, *our formal programme is to learn how to calculate $F(T, V)$.*

*NB:* We are talking exclusively about systems *in equilibrium*. If we also want to know how they get there, we need a lot more than just $F(V, T)$! Kinetic Theory dealt with such questions, Statistical Mechanics will *not*.

## 7.2. *The System and Its States*

What does it mean to have a microphysical model (description) of a physical system? And what exactly *is* a system? Well, *any physical system is a quantum-mechanical system and a quantum-mechanical system is something that can be in a number of quantum states*—we will call them *microstates*, they are defined by a set of quantum numbers (eigenvalues of a complete set of commuting variables).

*NB:* For systems with many degrees of freedom, e.g., many particles, we are talking about *collective* states of the system—these are *not* simply or necessarily direct superpositions of the states of individual particles. E.g., anticipating §11.9, a state of a box of ideal gas will be characterised by a set of numbers telling us how many particles occupy each single-particle state (characterised by discrete values of spin and momentum allowed in the box)—not by a list of which single-particle state each particle sits in.

Let us enumerate the system's microstates:

$$\alpha = 1,\ 2,\ 3,\ \dots,\ \Omega \ggg\gg 1 \tag{7.7}$$

(the total number of possible microstates is huge for a large system). For each such state, there is a certain probability of the system being in it:

$$p_1,\ p_2,\ p_3,\ \dots,\ p_\alpha,\ \dots,\ p_\Omega,\quad \sum_{\alpha=1}^{\Omega} p_\alpha = 1. \tag{7.8}$$

Each state has a certain energy:

$$E_1,\ E_2,\ E_3,\ \dots,\ E_\alpha,\ \dots,\ E_\Omega. \tag{7.9}$$

They might also have momenta, angular momenta, spins, and other quantum numbers.

If we knew all these things, we could then calculate various macrophysical quantities as averages over the distribution $\{p_\alpha\}$, e.g., the mean energy

$$\boxed{U = \langle E_\alpha \rangle = \sum_\alpha p_\alpha E_\alpha}\,. \tag{7.10}$$

Thus, it is easy to define macroscopic counterparts to quantities that already exist on the microscopic level, but it is not as yet clear what such thermodynamical quantities not obviously related to microphysics as $P$, $S$, $T$ are. In fact, the question of what pressure is can be cleared up without delay.

## 7.3. *Pressure*

The concept of pressure arises in connection with changing the volume of the system. In most of what follows (but not in Exercise 14.7), I will treat volume as an *exact external parameter* (as opposed to some mean property to be measured). Let us consider deformations that occur very very slowly. We know from Quantum Mechanics (e.g., Binney & Skinner 2013, §12.1) that if an external parameter (here volume) is changed slowly in an otherwise isolated system, the system will stay in the same eigenstate (say, $\alpha$) with its energy, $E_\alpha(V)$, changing slowly. This process is called *adiabatic* (we will learn soon that this meaning of "adiabatic" is equivalent to the familiar thermodynamical one).

Since the system's microstates $\{\alpha\}$ do not change in an adiabatic process, neither do their probabilities $\{p_\alpha\}$. The corresponding change in the mean energy is then

$$\mathrm{d}U_{\mathrm{ad}} = \left(\frac{\partial U}{\partial V}\right)_{p_1,\dots,p_\Omega} \mathrm{d}V = \sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial V}\,\mathrm{d}V. \tag{7.11}$$

But a slow change of energy in a system due exclusively to a change in its volume can be related to the work done *on* the system by whatever force is applied to effect the change. This work is, of course, equal to minus the work done *by* the system against that force:

$$\mathrm{d}U_{\mathrm{ad}} = \mathrm{d}W_{\mathrm{ad}} = -P\mathrm{d}V, \tag{7.12}$$

and so we may *define* pressure as

$$\boxed{P = -\sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial V} = -\left\langle \frac{\partial E_\alpha}{\partial V}\right\rangle}. \tag{7.13}$$

Similarly, in non-$PV$ systems,

$$f = \sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial L}, \qquad \text{tension}, \tag{7.14}$$

$$\boldsymbol{M} = -\sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial \boldsymbol{B}}, \quad \text{magnetisation, etc.} \tag{7.15}$$

Thus, if we know $\{p_\alpha\}$ and $\{E_\alpha\}$ (the latter as functions of $V$ or other external parameters), then we can calculate pressure and/or its non-$PV$ analogs.

It is clear that we cannot make any progress calculating $\{E_\alpha\}$ without specifying what our system is made of and how it is constituted. So the determination of the energies is a job for the microphysical (in general, quantum) theory. Normally, exact solution will only be possible for simple models (like the ideal gas). The amazing thing, however, is that *in equilibrium*, we will be able to determine $\{p_\alpha\}$ as functions of $\{E_\alpha\}$ in a completely general way—without having to solve a $\Omega$-dimensional Schrödinger equation for our system (which would clearly be a hopeless quest).

> *NB:* When I say "determine $\{p_\alpha\}$," what I really mean is *find a set of probabilities* $\{p_\alpha\}$ *such that upon their insertion into averages such (7.10) or (7.13), correct (experimentally verifiable) macroscopic quantities will be obtained.* This does *not* mean that these probabilities will literally be solutions of the Schrödinger equation for our system (many different sets of probabilities give the same averages, so, e.g., getting the correct mean energy does not imply—or, indeed, require—that the true probabilities be used).

To learn how to determine these $\{p_\alpha\}$, we will make a philosophical leap and learn to calculate things not on the basis of what we *know*, but on the basis of what we *don't know!*

## 8. Principle of Maximum Entropy

### 8.1. *Quantifying Ignorance*

In order to make progress, we will adopt the following, perhaps surprising (in view of your experience so far of school and undergraduate physics) attitude to the probabilities $\{p_\alpha\}$: we will think of them as measuring the degree of our *ignorance* about the true microstate that the system is really in. Just how ignorant we are depends on what information we do possess (or reliably expect to be able to obtain). The probabilities that we assign to various possible microstates of the system will then be the *likelihoods* for the system to be in those microstates, given the information that we have.[35]

*NB:* Defined like this, these probabilities reflect both the quantum uncertainty about the system's state and the more mundane fact that we have limited access to good information about the system. We deal this way simultaneously with the unknowable unknowns and the merely unavailable ones. How this all works in a more explicitly quantum language will be explained in §13.

8.1.1. *Complete Ignorance*

Suppose first that we know nothing at all about the system. Then the only fair way of assigning probabilities to microstates is to assume them all equally likely:

$$p_\alpha = \frac{1}{\Omega}. \tag{8.1}$$

This principle of fairness (in acknowledging that we have no basis for discriminating between microstates) can be given the status of a postulate, known as *the fundamental postulate of Statistical Mechanics*, a.k.a. *equal a priori probabilities postulate*, due to Boltzmann. Usually it is phrased as follows:

*For an* <u>*isolated*</u> *system* <u>*in equilibrium*</u>*, all microstates are equally likely.*

Here "isolated" means that the system is not in contact with anything—which is consistent with us knowing nothing about it (to know something, we must measure something, and to measure something, we would need to interfere with the system, which then would not be completely isolated anymore). "In equilibrium" means that $\{p_\alpha\}$ are not changing, the system is assumed to have settled in some statistically steady state.

In Boltzmann's Statistical Mechanics, this postulate serves as a starting point for the whole construction (see §12.1.2), but here we quickly move on to a more interesting situation.

8.1.2. *Some Knowledge*

The reason the no-knowledge case is *not* interesting is that ultimately, we are building this theory so we can *predict results of measurements*. This means that we do in fact expect to know something about our system—namely, the quantities that we intend to measure. Those will typically be macroscopic quantities, e.g., the mean energy:

$$U = \sum_\alpha p_\alpha E_\alpha. \tag{8.2}$$

Clearly, any particular measured value of $U$ will be consistent with lots of different (combinations of) microstates, so knowing $U$, while not generally consistent with equal probabilities (8.1), will not constrain the values of $p_\alpha$'s very strongly: indeed, there are $\Omega \ggg\ggg 1$ $p_\alpha$'s and only one equation (8.2) that they are required to satisfy (plus the normalisation $\sum_\alpha p_\alpha = 1$). We may be able to measure other quantities and so have more information in the form of equations like (8.2), but it is clear that the amount of information that we are ever likely to have (or want) falls hugely short of uniquely fixing every $p_\alpha$. This is good: it means that we do not need to know these probabilities well—just well enough to recover our measurable quantities.

[35] Adopting the view of probabilities as likelihoods, as opposed to *frequencies* with which the system is supposed to visit those microstates ("gambler's statistics," rather than "accountant's statistics"), is a controversial move, which will be further discussed in §12.2.

8.1.3. *Assignment of Likelihoods*

[Literature: Jaynes (2003), §11.4]

In order to make progress, we must find a way of *assigning values to* $\{p_\alpha\}$ *systematically, taking into account strictly the information that we have and nothing more.* We shall adopt the following algorithm (Jaynes 2003, §11.4).

We have $\Omega$ microstates and need to assign probabilities $p_1, \dots, p_\Omega$ to them, subject to $\sum_\alpha p_\alpha = 1$ and whatever constraints are imposed by our information.

• Choose some integer $\mathcal{N} \gg \Omega$ and embark on assigning $\mathcal{N}$ "quanta" of probability, each of magnitude $1/\mathcal{N}$, to the $\Omega$ microstates (imagine tossing $\mathcal{N}$ pennies into $\Omega$ boxes in an equiprobable way). After we have used up all $\mathcal{N}$ quanta, suppose we find

$$\begin{aligned} &\mathcal{N}_1 \text{ quanta in microstate } 1, \\ &\mathcal{N}_2 \text{ quanta in microstate } 2, \\ &\dots \\ &\mathcal{N}_\Omega \text{ quanta in microstate } \Omega, \end{aligned}$$

which corresponds to the assignment of probabilities

$$p_\alpha = \frac{\mathcal{N}_\alpha}{\mathcal{N}}, \quad \alpha = 1, \dots, \Omega. \tag{8.3}$$

• Check whether this set $\{p_\alpha\}$ satisfies the constraint(s) imposed by the available information, e.g., (8.2). If it does not, reject this assignment of probabilities and repeat the experiment. Keep going until a satisfactory set $\{p_\alpha\}$ is found.

Such a set is obviously not unique, but what will it most likely turn out to be as a result of this game? The number of ways $W$ in which an assignment (8.3) can be obtained is the number of ways of choosing $\mathcal{N}_1, \dots, \mathcal{N}_\Omega$ quanta out of a set of $\mathcal{N}$, viz.,

$$W = \frac{\mathcal{N}!}{\mathcal{N}_1! \cdots \mathcal{N}_\Omega!}. \tag{8.4}$$

All outcomes are equiprobable, so the most likely assignment $\{\mathcal{N}_\alpha\}$ is the one that *maximises* $W$ *subject to the constraints imposed by the available information.* It is possible to prove that this maximum is very sharp for large $\mathcal{N}$ (for a simple case of $\Omega = 2$, this is done in Exercise 8.1; for the more general case, see Schrödinger 1990). Since $\mathcal{N}$ is arbitrarily large, the most likely assignment is always the one that will actually occur.

Since we are at liberty to choose $\mathcal{N}$ as large as we like, we may assume that all $\mathcal{N}_\alpha \gg 1$ and use *Stirling's formula* to evaluate factorials:

$$\ln \mathcal{N}! = \mathcal{N} \ln \mathcal{N} - \mathcal{N} + O(\ln \mathcal{N}). \tag{8.5}$$

Then, using also $\sum_\alpha \mathcal{N}_\alpha = \mathcal{N}$,

$$\begin{aligned} \ln W &= \underbrace{\mathcal{N} \ln \mathcal{N} - \mathcal{N}}_{\sum_\alpha (\mathcal{N}_\alpha \ln \mathcal{N} - \cancel{\mathcal{N}_\alpha})} + O(\ln \mathcal{N}) - \sum_\alpha \left[\mathcal{N}_\alpha \ln \mathcal{N}_\alpha - \cancel{\mathcal{N}_\alpha} + O(\ln \mathcal{N}_\alpha)\right] \\ &= -\sum_\alpha \mathcal{N}_\alpha \ln \frac{\mathcal{N}_\alpha}{\mathcal{N}} + O(\ln \mathcal{N}) \\ &= -\mathcal{N} \left[\sum_\alpha p_\alpha \ln p_\alpha + O\left(\frac{\ln \mathcal{N}}{\mathcal{N}}\right)\right]. \end{aligned} \tag{8.6}$$

More precisely, if $\mathcal{N}$ and all $\mathcal{N}_\alpha \to \infty$ while $\mathcal{N}_\alpha/\mathcal{N} \to p_\alpha = \text{const}$, then there is a finite limit

$$\frac{1}{\mathcal{N}} \ln W \to -\sum_\alpha p_\alpha \ln p_\alpha \equiv S_{\rm G}. \tag{8.7}$$

This quantity is called the *Gibbs entropy*, or, in the context of information theory, the *Shannon entropy* (the "amount of ignorance" associated with the set of probabilities $\{p_\alpha\}$).

Maximising $W$ is the same as maximising $S_{\rm G}$, so the role of this quantity is that *the "fairest" assignment of probabilities $\{p_\alpha\}$ subject to some information will correspond to the maximum of $S_{\rm G}$ subject to the constraints imposed by that information.*

#### 8.1.4. *Some properties of Gibbs–Shannon Entropy*

1) $S_{\rm G}$ depends only on the probabilities $\{p_\alpha\}$, *not* on the quantum numbers (random variables) associated with the microstates that these probabilities describe (e.g., $E_\alpha$). This means that no change of variables (e.g., $E_\alpha \to f(E_\alpha)$) or rearrangement in the labelling of the microstates $\{\alpha\}$ can change $S_{\rm G}$. In other words, $S_{\rm G}$ is a property of the set of probabilities $\{p_\alpha\}$, not of the states $\{\alpha\}$.

2) Since $0 < p_\alpha \leqslant 1$, $S_{\rm G} \geqslant 0$ always. Note that $p_\alpha > 0$ because $p_\alpha = 0$ would mean that $\alpha$ is not an allowed state of the system; $p_\alpha = 1$ means that there is only one state that the system can be in, so it must be in it and then $S_{\rm G} = 0$—we have perfect knowledge $\Leftrightarrow$ zero ignorance.

3) Entropy is *additive:* essentially, when two systems are put together, the entropy of the composite system is the sum of the entropies of its two parts. This will discussed carefully in §10.1.

4) What is the maximum possible value of $S_{\rm G}$? The number of all possible distributions of $\mathcal{N}$ probability quanta over $\Omega$ microstates is $\Omega^{\mathcal{N}}$, which is, therefore, the maximum value that $W$ can take:[36]

$$W_{\rm max} = \Omega^{\mathcal{N}}. \tag{8.8}$$

Then the maximum possible value of $S_{\rm G}$ is

$$S_{\rm G,max} = \frac{1}{\mathcal{N}} \ln W_{\rm max} = \ln \Omega. \tag{8.9}$$

This value is attained when our ignorance about the system is total, which means that all microstates are, as far as we are concerned, equiprobable:

$$p_\alpha = \frac{1}{\Omega} \quad \Rightarrow \quad S_{\rm G} = -\sum_\alpha \frac{1}{\Omega} \ln \frac{1}{\Omega} = \ln \Omega = S_{\rm G,max}. \tag{8.10}$$

---

In this context, the Shannon (1948) definition of the *information content* of a probability distribution is

$$I(p_1, \dots, p_\Omega) = S_{\rm G,max} - S_{\rm G}(p_1, \dots, p_\Omega) = \ln \Omega + \sum_\alpha p_\alpha \ln p_\alpha. \tag{8.11}$$

Maximising $S_{\rm G}$ is the same as minimising $I$. Shannon's paper (Shannon 1948) is an excellent read. I will come back to his results in §8.1.5.

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**Exercise 8.1. Tossing a Coin.** This example illustrates the scheme for assignment of *a priori* probabilities to microstates discussed in §8.1.3.

[36] At finite $\mathcal{N}$, this is not a sharp bound for (8.4), but its gets sharper for $\mathcal{N} \gg 1$.

Suppose we have a system that only has two states, $\alpha = 1, 2$, and no further information about it is available. We shall assign probabilities to these states in a fair and balanced way: by flipping a coin $\mathcal{N} \gg 1$ times, recording the number of heads $\mathcal{N}_1$ and tails $\mathcal{N}_2$ and declaring that the probabilities of the two states are $p_1 = \mathcal{N}_1/\mathcal{N}$ and $p_2 = \mathcal{N}_2/\mathcal{N}$.

(a) Calculate the number of ways, $W$, in which a given outcome $\{\mathcal{N}_1, \mathcal{N}_2\}$ can happen, find its maximum and prove therefore that the most likely assignment of probabilities will be $p_1 = p_2 = 1/2$. What is the Gibbs entropy of this system?

(b) Show that for a large number of coin tosses, this maximum is sharp. Namely, show that the number of ways $W(m)$ in which you can get an outcome with $\mathcal{N}/2 \pm m$ heads (where $\mathcal{N} \gg m \gg 1$) is

$$\frac{W(m)}{W(0)} \approx \exp\left(-2m^2/\mathcal{N}\right), \tag{8.12}$$

where $W(0)$ corresponds to the most likely situation found in (a); hence argue that the relative width of the maximum around $p_{1,2} = 1/2$ is $\delta p \sim 1/\sqrt{\mathcal{N}}$.

---

### 8.1.5. *Shannon's Theorem*

[Literature: Shannon (1948), §6; Jaynes (2003), §11.3; Binney & Skinner (2013), §6.3.2]

In §8.1.3, I argued that, in order to achieve the "fairest" and most unbiased assignment of probabilities $p_\alpha$ to microstates $\alpha$, one must maximise the function

$$S_G(p_1, \dots, p_\Omega) = -\sum_\alpha p_\alpha \ln p_\alpha \tag{8.13}$$

(called Gibbs entropy, Shannon entropy, "information entropy," measure of uncertainty, etc.). I did this by presenting a reasonable and practical scheme for assigning probabilities, which I asked you to agree was the fairest imaginable. In the spirit of formalistic nit-picking, you might be tempted to ask whether the function (8.13) is in any sense unique—could we have invented other "fair games" leading to different definitions of entropy? Here is an argument that addresses this question.

Faced with some set of probabilities $\{p_\alpha\}$ ("a distribution"), let us seek to define a function $H(p_1, \dots, p_\Omega)$ that would measure the uncertainty associated with this distribution. In order to be a suitable such measure, $H$ must satisfy certain basic properties:

1) $H$ should be a continuous function of $p_\alpha$'s (i.e., changing $p_\alpha$'s a little should not dramatically change the measure of uncertainty associated with them);

2) $H$ should be symmetric with respect to permutations of $\{p_\alpha\}$ (i.e., it should not matter in what order we list the microstates);

3) for any set of probabilities $\{p_\alpha\}$ that are not all equal,

$$H(p_1, \dots, p_\Omega) < H\left(\frac{1}{\Omega}, \dots, \frac{1}{\Omega}\right) \equiv H_\Omega \tag{8.14}$$

(the distribution with all equal probabilities corresponds to maximum uncertainty);

4) if $\Omega' > \Omega$, $H_{\Omega'} > H_\Omega$ (more equiprobable microstates $\Rightarrow$ more uncertainty);

5) $H$ should be *additive* and *independent of how we count the microstates*, in the following sense. If the choice of a microstate is broken down into two successive choices—first a subgroup, then the individual state—the total $H$ should be a weighted sum of individual values of

$H$ associated with each subgroup. Namely, split the microstates into groups:

$$\alpha = \underbrace{1,\dots,m_1}_{\substack{\text{group}\\ i=1\\ \downarrow\\ \text{probability}\\ w_1}},\underbrace{m_1+1,\dots,m_1+m_2}_{\substack{\text{group}\\ i=2\\ \downarrow\\ \text{probability}\\ w_2}},\dots,\underbrace{\sum_{i=1}^{M-1} m_i+1,\dots,\sum_{i=1}^{M} m_i = \Omega}_{\substack{\text{group}\\ i=M\\ \downarrow\\ \text{probability}\\ w_M}}. \tag{8.15}$$

Clearly, $w_i$ is the sum of $p_\alpha$'s for the states that are in the group $i$. Within each group, we can assign *conditional* probabilities to all microstates in that group, viz., the probability for the system to be in microstate $\alpha$ within group $i$ if it is given that the system is in one of the microstates in that group, is

$$p_\alpha^{(i)} = \frac{p_\alpha}{w_i}. \tag{8.16}$$

We then want $H$ to satisfy

$$\begin{aligned}\underbrace{H(p_1,\dots,p_\Omega)}_{\substack{\text{total}\\ \text{uncertainty}}} &= \underbrace{H(w_1,\dots,w_M)}_{\substack{\text{uncertainty in}\\ \text{the}\\ \text{distribution}\\ \text{of groups}}} + w_1\underbrace{H(p_1^{(1)},\dots,p_{m_1}^{(1)})}_{\substack{\text{uncertainty}\\ \text{within}\\ \text{group 1}}} + w_2\underbrace{H(p_{m_1+1}^{(2)},\dots,p_{m_1+m_2}^{(2)})}_{\substack{\text{uncertainty}\\ \text{within}\\ \text{group 2}}}+\dots\\ &= H(w_1,\dots,w_M) + w_1 H\left(\frac{p_1}{w_1},\dots,\frac{p_{m_1}}{w_1}\right) + w_2 H\left(\frac{p_{m_1+1}}{w_2},\dots,\frac{p_{m_1+m_2}}{w_2}\right)+\dots\end{aligned} \tag{8.17}$$

**Theorem.** The only function $H$ with these properties is

$$H(p_1,\dots,p_\Omega) = -k\sum_\alpha p_\alpha \ln p_\alpha, \tag{8.18}$$

where $k>0$ is a constant.

**Proof.** Let us first consider a special case of equal probabilities:

$$\text{all } p_\alpha = \frac{1}{\Omega} \quad\Rightarrow\quad w_i = \frac{m_i}{\Omega},\quad p_\alpha^{(i)} = \frac{p_\alpha}{w_i} = \frac{1}{m_i}. \tag{8.19}$$

Then the criterion (8.17) becomes

$$H_\Omega \equiv H\left(\frac{1}{\Omega},\dots,\frac{1}{\Omega}\right) = H(w_1,\dots,w_M) + \sum_{i=1}^M w_i \underbrace{H\left(\frac{1}{m_i},\dots,\frac{1}{m_i}\right)}_{\equiv H_{m_i}}. \tag{8.20}$$

Therefore,

$$H(w_1,\dots,w_M) = H_\Omega - \sum_{i=1}^M w_i H_{m_i}. \tag{8.21}$$

Now consider the special case of this formula for the situation in which all $m_i = m$ are the same. Then

$$\Omega = mM,\quad w_i = \frac{m}{\Omega}, \tag{8.22}$$

and (8.21) becomes

$$H_M = H_{mM} - H_m. \tag{8.23}$$

This is a functional equation for $H_m \equiv f(m)$:

$$f(mn) = f(m) + f(n). \tag{8.24}$$

**Lemma.** The only monotonically increasing[37] function that satisfies (8.24) is

$$f(m) = k \ln m, \tag{8.25}$$

where $k$ is a positive constant.

---

**Proof.** For any integers $m, n > 1$, we can always find integers $r$ and (an arbitrarily large) $s$ such that

$$\frac{r}{s} < \frac{\ln m}{\ln n} < \frac{r+1}{s} \quad \Rightarrow \quad n^r < m^s < n^{r+1}. \tag{8.26}$$

As $f$ is a monotonically increasing function,

$$f(n^r) < f(m^s) < f(n^{r+1}). \tag{8.27}$$

But (8.24) implies $f(n^r) = rf(n)$, so the above inequality becomes

$$rf(n) < sf(m) < (r+1)f(n) \quad \Rightarrow \quad \frac{r}{s} < \frac{f(m)}{f(n)} < \frac{r+1}{s}. \tag{8.28}$$

The inequalities (8.26) and (8.28) imply

$$\left|\frac{f(m)}{f(n)} - \frac{\ln m}{\ln n}\right| < \frac{1}{s} \quad \Rightarrow \quad \left|\frac{f(m)}{\ln m} - \frac{f(n)}{\ln n}\right| < \frac{1}{s}\frac{f(n)}{\ln m} \to 0 \tag{8.29}$$

because $s$ can be chosen arbitrarily large. Therefore

$$\frac{f(m)}{\ln m} = \frac{f(n)}{\ln n} = \text{const} = k, \quad \text{q.e.d.} \tag{8.30}$$

The constant is positive, $k > 0$, because $f(m)$ is supposed to be *in*creasing.

---

Thus, we have proven

$$H_\Omega = k \ln \Omega. \tag{8.31}$$

Substituting this into (8.21), we get

$$H(w_1, \dots, w_M) = k\left(\ln \Omega - \sum_{i=1}^{M} w_i \ln m_i\right) = -k\sum_{i=1}^{M} w_i \ln \frac{m_i}{\Omega} = -k\sum_{i=1}^{M} w_i \ln w_i. \tag{8.32}$$

But $\{m_i\}$ and, therefore, $\{w_i\}$, were chosen in a completely general way, subject only to $\sum_i m_i = \Omega$, or $\sum_i w_i = 1$. Therefore, with equal validity,[38]

$$H(p_1, \dots, p_\Omega) = -k\sum_\alpha p_\alpha \ln p_\alpha, \quad \text{q.e.d.} \tag{8.33}$$

Choosing $k = 1$ gives us $H = S_{\rm G}$, which we called the Gibbs (or Gibbs–Shannon) entropy (§8.1.3); $k = k_{\rm B}$ gives $H = S$, the conventional thermodynamical entropy (in thermal equilibrium); $k = 1/\ln 2$ is the convention for Shannon entropy as used in measuring information content.

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## 8.2. *Method of Lagrange Multipliers*

Mathematically, how does one maximise a function of $\Omega$ variables, say, $S_{\rm G}(p_1, \dots, p_\Omega)$, subject to some constraint that has a general form

$$F(p_1, \dots, p_\Omega) = 0, \tag{8.34}$$

e.g., (8.2), which we can write as $F(p_1, \dots, p_\Omega) \equiv \sum_\alpha p_\alpha E_\alpha - U = 0$?

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[37] Which it must be because we need $H_{\Omega'} > H_\Omega$ for $\Omega' > \Omega$; see condition 4 on the $H$ function.

[38] Technically speaking, we have only obtained this formula for $p_\alpha$'s (or $w_i$'s) that are rational numbers. This is OK: if $p_\alpha$'s are irrational, they can be approximated arbitrarily well by rationals and so $H$ still has to be given by (8.33) because $H$ must be continuous according to Criterion 1 imposed on it at the beginning of this section.

At the point of maximum (or, to be precise, extremum) of $S_{\rm G}$,

$$\mathrm{d}S_{\rm G} = \frac{\partial S_{\rm G}}{\partial p_1}\,\mathrm{d}p_1 + \dots + \frac{\partial S_{\rm G}}{\partial p_\Omega}\,\mathrm{d}p_\Omega = 0, \tag{8.35}$$

but the increments $\{\mathrm{d}p_\alpha\}$ are not independent because $\{p_\alpha\}$ are only allowed to change subject to the constraint (8.34). Thus, $F$ cannot change:

$$\mathrm{d}F = \frac{\partial F}{\partial p_1}\,\mathrm{d}p_1 + \dots + \frac{\partial F}{\partial p_\Omega}\,\mathrm{d}p_\Omega = 0. \tag{8.36}$$

From this equation, we can calculate one of $\mathrm{d}p_\alpha$'s in terms of the others—it can just as well be the first one:

$$\mathrm{d}p_1 = -\left(\frac{\partial F/\partial p_2}{\partial F/\partial p_1}\,\mathrm{d}p_2 + \dots + \frac{\partial F/\partial p_\Omega}{\partial F/\partial p_1}\,\mathrm{d}p_\Omega\right). \tag{8.37}$$

Substitute this into (8.35):

$$\mathrm{d}S_{\rm G} = \left(\frac{\partial S_{\rm G}}{\partial p_2} - \underbrace{\frac{\partial S_{\rm G}/\partial p_1}{\partial F/\partial p_1}}_{\equiv\,\lambda}\frac{\partial F}{\partial p_2}\right)\mathrm{d}p_2 + \dots + \left(\frac{\partial S_{\rm G}}{\partial p_\Omega} - \underbrace{\frac{\partial S_{\rm G}/\partial p_1}{\partial F/\partial p_1}}_{\equiv\,\lambda}\frac{\partial F}{\partial p_\Omega}\right)\mathrm{d}p_\Omega. \tag{8.38}$$

In this equation, $\mathrm{d}p_2, \dots, \mathrm{d}p_\Omega$ are now all independent (we only had one constraint on $\Omega$ variables, so $\Omega-1$ of them of them can be independently varied). Therefore, (8.38) implies that

$$\frac{\partial S_{\rm G}}{\partial p_\alpha} - \lambda\,\frac{\partial F}{\partial p_\alpha} = 0 \quad \text{for} \quad \alpha = 2, \dots, \Omega, \tag{8.39}$$

where, by definition of $\lambda$,

$$\frac{\partial S_{\rm G}}{\partial p_1} - \lambda\,\frac{\partial F}{\partial p_1} = 0. \tag{8.40}$$

So, we now have $\Omega+1$ variables, $p_1$, ..., $p_\Omega$, $\lambda$, and $\Omega+1$ equations for them: (8.39), (8.40) and (8.34):

$$\frac{\partial S_{\rm G}}{\partial p_\alpha} - \lambda\,\frac{\partial F}{\partial p_\alpha} = 0 \quad \text{for} \quad \alpha = 1, \dots, \Omega, \tag{8.41}$$

$$F(p_1, \dots, p_\Omega) = 0. \tag{8.42}$$

But these are exactly the equations that we would get if we wanted to *maximise* $S_{\rm G} - \lambda F$ *with respect to* $p_1$, ..., $p_\Omega$, $\lambda$, *and with no constraints:*

$$\mathrm{d}(S_{\rm G} - \lambda F) = \sum_\alpha \left(\frac{\partial S_{\rm G}}{\partial p_\alpha} - \lambda\,\frac{\partial F}{\partial p_\alpha}\right)\mathrm{d}p_\alpha - F\mathrm{d}\lambda = 0. \tag{8.43}$$

This, then, is the method for conditional maximising (extremising) a function subject to a constraint: add to it that constraint multiplied by $-\lambda$ and maximise the resulting function unconditionally, with respect to the original variables and $\lambda$. The additional variable $\lambda$ is called the *Lagrange multiplier*.

The method is easily generalised to the case of several constraints: suppose, instead of one constraint (8.34), we have $m$ of them:

$$F_i(p_1, \dots, p_\Omega) = 0, \quad i = 1, \dots, m. \tag{8.44}$$

To maximise $S_{\rm G}$ subject to these, introduce $m$ Lagrange multipliers $\lambda_1$, ..., $\lambda_m$ and maximise unconditionally

$$\boxed{S_\mathrm{G} - \sum_i \lambda_i F_i \to \max} \tag{8.45}$$

with respect to $\Omega + m$ variables $p_1, \dots, p_\Omega, \lambda_1, \dots \lambda_m$. Obviously, in order to have a solution, we must have $m < \Omega$—fewer constraints than the system has microstates. But this is not going to be a problem as the number of microstates is usually huge, while the number of things we can possibly hope (or want) to measure very finite indeed.

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### 8.3. *Test of the Method: Isolated System*

Before we do anything nontrivial with our newly acquired technique, let us make sure that we can recover the one case for which we know the solution: equal probabilities for microstates of a system about which we know nothing.

If we know nothing, the only constraint on the probabilities is

$$\sum_\alpha p_\alpha = 1. \tag{8.46}$$

Maximising $S_\mathrm{G}$ subject to this constraint is equivalent to unconditionally maximising

$$S_\mathrm{G} - \lambda \left( \sum_\alpha p_\alpha - 1 \right) \to \max. \tag{8.47}$$

This gives

$$\mathrm{d}S_\mathrm{G} - \lambda \sum_\alpha \mathrm{d}p_\alpha - \left( \sum_\alpha p_\alpha - 1 \right) \mathrm{d}\lambda = 0. \tag{8.48}$$

Using the Gibbs formula (8.7) for $S_\mathrm{G}$, we have

$$\mathrm{d}S_\mathrm{G} = -\sum_\alpha (\ln p_\alpha + 1)\, \mathrm{d}p_\alpha \tag{8.49}$$

and so (8.48) becomes

$$-\sum_\alpha \underbrace{(\ln p_\alpha + 1 + \lambda)}_{=0} \mathrm{d}p_\alpha - \underbrace{\left( \sum_\alpha p_\alpha - 1 \right)}_{=0} \mathrm{d}\lambda = 0. \tag{8.50}$$

In order to satisfy this equation, we must set the coefficient in front of $\mathrm{d}p_\alpha$ to zero, which gives

$$p_\alpha = e^{-(1+\lambda)}. \tag{8.51}$$

Setting also the coefficient in front of $\mathrm{d}\lambda$ to zero (this is just the constraint (8.46)), we find

$$\sum_\alpha e^{-(1+\lambda)} = \Omega\, e^{-(1+\lambda)} = 1 \quad \Rightarrow \quad e^{-(1+\lambda)} = \frac{1}{\Omega}. \tag{8.52}$$

Thus, we recover the equal-probabilities distribution (8.1), with $S_\mathrm{G}$ for this distribution taking the maximum possible value [see (8.10)]:

$$p_\alpha = \frac{1}{\Omega}, \quad S_\mathrm{G} = \ln \Omega, \tag{8.53}$$

the state of maximum ignorance. Our method works.

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## 9. Canonical Ensemble

## 9.1. *Gibbs Distribution*

We are now going to implement the programme of deriving the probability distribution resulting from maximising entropy subject to a single physical constraint: a fixed value of mean energy,

$$\sum_\alpha p_\alpha E_\alpha = U. \tag{9.1}$$

The set of realisations of a system described by this probability distribution is called the *canonical ensemble*, introduced by J. W. Gibbs (1839–1903), a great American physicist whose name will loom large in everything that follows. Constraints other than (or in addition to) (9.1) will define different ensembles, some of which will be discussed later (see §14 and Exercise 14.7).

As explained in §8.2, in order to find $\{p_\alpha\}$, we must maximise $S_\mathrm{G} = -\sum_\alpha p_\alpha \ln p_\alpha$ subject to the constraint (9.1) and to $\sum_\alpha p_\alpha = 1$ [see (8.46)]. This means that we need two Lagrange multipliers, which I will call $\lambda$ and $\beta$, and an unconditional maximum

$$S_\mathrm{G} - \lambda\left(\sum_\alpha p_\alpha - 1\right) - \beta\left(\sum_\alpha p_\alpha E_\alpha - U\right) \to \max \tag{9.2}$$

with respect to $p_1, p_2, \dots p_\Omega, \lambda$ and $\beta$. Taking the differential of this (varying $p_\alpha$'s, $\lambda$ and $\beta$),

$$\mathrm{d}S_\mathrm{G} - \lambda \sum_\alpha \mathrm{d}p_\alpha - \left(\sum_\alpha p_\alpha - 1\right)\mathrm{d}\lambda - \beta\sum_\alpha E_\alpha \mathrm{d}p_\alpha - \left(\sum_\alpha p_\alpha E_\alpha - U\right)\mathrm{d}\beta = 0, \tag{9.3}$$

and using (8.49) for $\mathrm{d}S_\mathrm{G}$, we get

$$-\sum_\alpha \underbrace{(\ln p_\alpha + 1 + \lambda + \beta E_\alpha)}_{=0}\mathrm{d}p_\alpha - \underbrace{\left(\sum_\alpha p_\alpha - 1\right)}_{=0}\mathrm{d}\lambda - \underbrace{\left(\sum_\alpha p_\alpha E_\alpha - U\right)}_{=0}\mathrm{d}\beta = 0. \tag{9.4}$$

Setting the coefficients in front of $\mathrm{d}p_\alpha$ (which are all now independent!) individually to zero, we get

$$p_\alpha = e^{-1-\lambda-\beta E_\alpha}. \tag{9.5}$$

The Lagrange multiplier $\lambda$, or, equivalently, the normalisation constant $e^{-(1+\lambda)}$, is obtained from

$$\sum_\alpha p_\alpha - 1 = 0 \quad\Rightarrow\quad e^{-(1+\lambda)}\sum_\alpha e^{-\beta E_\alpha} = 1 \quad\Rightarrow\quad e^{-(1+\lambda)} = \frac{1}{Z(\beta)}, \tag{9.6}$$

where

$$Z(\beta) = \sum_\alpha e^{-\beta E_\alpha} \tag{9.7}$$

is called the *partition function* ($Z$ for "Zustandssumme," its German name).[39] Then the desired probability distribution (9.5) is

$$\boxed{p_\alpha = \frac{e^{-\beta E_\alpha}}{Z(\beta)}}, \tag{9.8}$$

---

[39]Note the upcoming physical interpretation of the partition function as the number of microstates effectively available to the system at a given temperature (see §11.9).

known as the *Gibbs (canonical) distribution*. Finally, the second Lagrange multiplier $\beta$ is found from the constraint (9.1),

$$\sum_\alpha p_\alpha E_\alpha = \frac{1}{Z(\beta)} \sum_\alpha E_\alpha e^{-\beta E_\alpha} = -\frac{\partial \ln Z}{\partial \beta} = U. \tag{9.9}$$

The latter equality gives us an implicit equation for $\beta$ in terms of $U$.

*NB:* Everything here is also a function of a number of other parameters that we viewed as exactly fixed: e.g., volume $V$, number of particles $N$—they enter via the dependence of the energy levels on them, $E_\alpha = E_\alpha(V, N)$. If we instead view them *not* as fixed parameters but as random quantities with some measurable average values, then we will obtain different ensembles: e.g., the *grand canonical ensemble*, used to describe open systems, where the mean number of particles $\langle N \rangle$ provides a constraint on maximising entropy (§14), or the so-called "pressure ensemble," where it is the average volume of the system, $\langle V \rangle$, that is considered a quantity to be measured (Exercise 14.7).

### 9.2. *Construction of Thermodynamics*

[Literature: Schrödinger (1990), Ch. II]

I am going to show you that we have solved the problem posed in §7: how to work out all thermodynamically relevant quantities (in particular, free energy) and relationships from just knowing the energy levels $\{E_\alpha\}$ of a given system. To do this, we first need to establish what $\beta$ means and then how to calculate the thermodynamical entropy $S$ and pressure $P$.

The Gibbs entropy in the equilibrium given by the Gibbs distribution (9.8) is

$$S_G = -\sum_\alpha p_\alpha \ln p_\alpha = -\sum_\alpha p_\alpha(-\beta E_\alpha - \ln Z) = \beta U + \ln Z. \tag{9.10}$$

Therefore, in equilibrium,[40]

$$\begin{aligned} \mathrm{d}S_G &= \beta \mathrm{d}U + U\mathrm{d}\beta + \frac{\mathrm{d}Z}{Z} \\ &= \beta \mathrm{d}U + \cancel{U\mathrm{d}\beta} + \sum_\alpha \underbrace{\frac{e^{-\beta E_\alpha}}{Z}}_{=p_\alpha}(-\beta \mathrm{d}E_\alpha - \cancel{E_\alpha \mathrm{d}\beta}) \\ &= \beta\left(\mathrm{d}U - \sum_\alpha p_\alpha \mathrm{d}E_\alpha\right). \end{aligned} \tag{9.11}$$

Since $E_\alpha = E_\alpha(V)$ (we will hold $N$ to be unchangeable for now), $\mathrm{d}E_\alpha = (\partial E_\alpha/\partial V)\mathrm{d}V$. Recalling (7.13), we then identify the second term inside the bracket in (9.11) as $P\mathrm{d}V$, so

$$\mathrm{d}S_G = \beta(\mathrm{d}U + P\mathrm{d}V) = \beta \mathrm{d}Q_{\mathrm{rev}}, \tag{9.12}$$

where $\mathrm{d}Q_{\mathrm{rev}} = \mathrm{d}U - \mathrm{d}W_{\mathrm{ad}}$ is the *definition* of reversible heat, the difference between the change in internal energy and the adiabatic work $\mathrm{d}W_{\mathrm{ad}} = -P\mathrm{d}V$ done on the system. The left-hand side of (9.12) is a full differential of $S_G$, which is clearly a function of state.

[40]Here the differential of $S_G$ is between different equilibrium states, i.e., we vary external parameters and constraints, viz., $V$ and $U$—not the probability distribution, as we did in (9.3) in order to find the equilibrium state. The $S_G$ that we vary here, given by (9.10), is already the maximum $S_G$ (for any given $V$, $U$) that we found in §9.1.

So we have found that $\beta$ *is an integrating factor of heat in thermal equilibrium—Kelvin's definition of (inverse) thermodynamical temperature!*

Thus, it must be the case that

$$\boxed{\beta = \frac{1}{k_{\rm B}T}}\,, \tag{9.13}$$

i.e., $1/\beta$ differs from the thermodynamical temperature at most by a constant factor, which we choose to be the Boltzmann constant simply to convert from energy units ($\beta$ multiplies $E_\alpha$ in the exponentials, so its units are inverse energy) to degrees Kelvin, a historical (in)convenience. Then (9.12) immediately implies the relationship between the thermodynamical entropy $S$ and the Gibbs–Shannon entropy $S_{\rm G}$:

$$\boxed{S = k_{\rm B}S_{\rm G}}\,. \tag{9.14}$$

(see §§9.3 and 9.4 for a more formal proof of these results).

With (9.13) and (9.14), (9.12) turns into the familiar *fundamental equation of thermodynamics:*

$$\boxed{T{\rm d}S = {\rm d}U + P{\rm d}V}\,. \tag{9.15}$$

We are done: introducing as usual the *free energy*

$$F = U - TS, \tag{9.16}$$

we can calculate everything (see §7.1): equation of state, entropy, energy, etc.:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad U = F + TS, \dots \tag{9.17}$$

The progress we have made is that we now know the explicit expression for $F$ in terms of energy levels of the systems: namely, combining (9.10), (9.13) and (9.14), we get

$$\frac{S}{k_{\rm B}} = \frac{U}{k_{\rm B}T} + \ln Z, \tag{9.18}$$

whence, via (9.16),

$$\boxed{F = -k_{\rm B}T\ln Z, \quad \text{where} \quad Z = \sum_\alpha e^{-E_\alpha/k_{\rm B}T}}\,. \tag{9.19}$$

This means, by the way, that *if we know the partition function, we know about the system everything that is needed to describe its equilibrium thermodynamics.*

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Note that from (9.19) follows a nice way to write the Gibbs distribution (9.8):

$$Z = e^{-\beta F} \quad \Rightarrow \quad p_\alpha = \frac{e^{-\beta E_\alpha}}{Z} = e^{\beta(F-E_\alpha)}. \tag{9.20}$$

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### 9.3. *Some Mathematical Niceties*

[Literature: Schrödinger (1990), Ch. II]

If you thought the derivation of (9.13) and (9.14) in §9.2 was a little cavalier, mathematically, here is a more formal proof.

We had derived, using only the principle of maximum entropy (8.7) (Gibbs–Shannon entropy, which at that point had nothing to do with the thermodynamic entropy, heat engines or any of that) and the definition of pressure (7.13), that [see (9.12)]

$${\rm d}S_{\rm G} = \beta{\rm d}Q_{\rm rev}. \tag{9.21}$$

From Thermodynamics, we knew the *thermodynamic* entropy $S$, *thermodynamic* temperature $T$ and the reversible heat to be related by

$$dS = \frac{1}{T}\,dQ_{\rm rev}. \tag{9.22}$$

Therefore,

$$dS = \frac{1}{\beta T}\,dS_{\rm G}. \tag{9.23}$$

Since the left-hand side of this equation is a full differential, so is the right-hand side. Therefore, $1/\beta T$ is a function of $S_{\rm G}$ only:

$$\frac{1}{\beta T} = f(S_{\rm G}) \quad\Rightarrow\quad dS = f(S_{\rm G})dS_{\rm G} \quad\Rightarrow\quad S = \varphi(S_{\rm G}), \tag{9.24}$$

i.e., thermodynamic entropy is some function (obtained by integration of $f$) of Gibbs entropy and only of it.

But $S$ is an additive function (we know this from Thermodynamics) and so is $S_{\rm G}$ (see proof in §10.1). Therefore, if we consider two systems, 1 and 2, and the combined system 12, we must have

$$S_{\rm G,1} + S_{\rm G,2} = S_{\rm G,12}, \quad S_1 + S_2 = S_{12}, \tag{9.25}$$

whence

$$\varphi_1(S_{\rm G,1}) + \varphi_2(S_{\rm G,2}) = \varphi_{12}(S_{\rm G,1} + S_{\rm G,2}), \tag{9.26}$$

whence

$$\varphi_1'(S_{\rm G,1}) = \varphi_{12}'(S_{\rm G,1} + S_{\rm G,2}), \tag{9.27}$$
$$\varphi_2'(S_{\rm G,2}) = \varphi_{12}'(S_{\rm G,1} + S_{\rm G,2}). \tag{9.28}$$

Therefore,

$$\varphi_1'(S_{\rm G,1}) = \varphi_2'(S_{\rm G,2}) = {\rm const} \equiv k_{\rm B} \tag{9.29}$$

("separation constant"), giving

$$\varphi'(S_{\rm G}) = f(S_{\rm G}) = k_{\rm B} \quad\Rightarrow\quad \frac{1}{k_{\rm B}T} = f(S_{\rm G}) = k_{\rm B} \quad\Rightarrow\quad \beta = \frac{1}{k_{\rm B}T}, \tag{9.30}$$

q.e.d., the desired result (9.13). This implies, finally [see (9.24)],

$$dS = k_{\rm B}dS_{\rm G} \quad\Rightarrow\quad S = k_{\rm B}S_{\rm G} + {\rm const}. \tag{9.31}$$

Setting const = 0 gives (9.14), q.e.d. It remains to discuss this choice of the integration constant, which has a physical meaning.

### 9.4. *Third Law*

[Literature: Schrödinger (1990), Ch. III]

From (9.10), the Gibbs entropy in thermal equilibrium is

$$S_{\rm G} = \ln\sum_\alpha e^{-\beta E_\alpha} + \beta\,\frac{\sum_\alpha E_\alpha e^{-\beta E_\alpha}}{\sum_\alpha e^{-\beta E_\alpha}}. \tag{9.32}$$

Consider what happens to this quantity in the limit $T \to 0$, or $\beta \to \infty$. Suppose the lowest energy level is $E_1$ and the lowest $m$ microstates have this energy, viz.,

$$E_\alpha = E_1 \text{ for } \alpha = 1, \dots, m \quad\text{and}\quad E_\alpha > E_1 \text{ for } \alpha > m. \tag{9.33}$$

Then

$$
\begin{aligned}
S_{\mathrm{G}} &= \ln\left(me^{-\beta E_1} + \sum_{\alpha>m} e^{-\beta E_\alpha}\right) + \beta\,\frac{mE_1 e^{-\beta E_1} + \sum_{\alpha>m} E_\alpha e^{-\beta E_\alpha}}{me^{-\beta E_1} + \sum_{\alpha>m} e^{-\beta E_\alpha}},\\
&= \ln\left[me^{-\beta E_1}\left(1 + \frac{1}{m}\sum_{\alpha>m} e^{-\beta(E_\alpha - E_1)}\right)\right] + \beta E_1\,\frac{1 + \frac{1}{m}\sum_{\alpha>m}\frac{E_\alpha}{E_1} e^{-\beta(E_\alpha-E_1)}}{1 + \frac{1}{m}\sum_{\alpha>m} e^{-\beta(E_\alpha-E_1)}}\\
&\approx \ln m - \cancel{\beta E_1} + \frac{1}{m}\sum_{\alpha>m} e^{-\beta(E_\alpha-E_1)} + \beta E_1\left[\cancel{1} + \frac{1}{m}\sum_{\alpha>m}\left(\frac{E_\alpha}{E_1} - 1\right) e^{-\beta(E_\alpha-E_1)}\right]\\
&= \ln m + \frac{1}{m}\sum_{\alpha>m}\left[1 + \beta(E_\alpha - E_1)\right] e^{-\beta(E_\alpha-E_1)}.
\end{aligned}
\tag{9.34}
$$

The second term is exponentially small as $\beta \to \infty$, so

$$\boxed{S_{\mathrm{G}} \to \ln m \quad \text{as} \quad T \to 0}\,, \tag{9.35}$$

where $m$ is the degeneracy of the lowest energy level. Physically, this makes sense: at zero temperature, the system will be in one of its $m$ available lowest-energy states, all of which have equal probability.

Setting const $= 0$ in (9.31) means that also the thermodynamic entropy

$$S \to k_{\mathrm{B}} \ln m \quad \text{as} \quad T \to 0. \tag{9.36}$$

Recall that *the 3-rd Law of Thermodynamics* said that $S \to 0$ as $T \to 0$. This is not a contradiction because $k_{\mathrm{B}} \ln m$ is very small compared to typical values that $S$ can have: indeed, since $S$ is additive, it will generally be proportional to the number of particles in the system, $S \propto k_{\mathrm{B}} N$ (see §11.10), whereas obviously $\ln m \ll N$ except for very strange systems. Thus, *the choice* const $= 0$ *in (9.31) is basically the statement of the 3-rd Law.* You will find further discussion of this topic in Chapter III of Schrödinger (1990).

*NB:* In any event, these details do not matter very much because what is important is that the constant in (9.31) is a constant, independent of the parameters of the system, so all entropy *differences* are independent of it—and related via $k_{\mathrm{B}}$ when expressed in terms of $S$ and $S_{\mathrm{G}}$.

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## 9.5. *Part I Obviated, Road Ahead Clear*

Thus, I have proved that the statistical-mechanical $T$ and $S$ are the same as the thermodynamical $T$ and $S$. This was a nice exercise, but, strictly speaking, unnecessary. Instead, I could have *defined*

$$S \equiv k_{\mathrm{B}} S_{\mathrm{G}} \quad \text{and} \quad T \equiv \frac{1}{k_{\mathrm{B}}\beta} \tag{9.37}$$

(with a historical factor of $k_{\mathrm{B}}$ to show respect for tradition) and then *constructed all of Thermodynamics as a consequence of Statistical Mechanics*, without ever having to go through all those heat engines, Carnot cycles, etc. Indeed, with the definitions (9.37), we get the entire thermodynamic calculus, based on (9.15), the specific expression (9.19) for $F$ (or $Z$), and the expressions (9.17) for everything else in terms of $F$.

So, the way it all has been presented to you is *chronological*, rather than *logical*:[41] Thermodynamics was worked out in the 19-th century, before Statistical Mechanics finally emerged in its modern form in the early 20-th. Logically, we no longer need a separate construction of Thermodynamics, except as an intellectual exercise and a beautiful example of how to set up an empirical theory of physical phenomena whose microscopic nature one does not yet understand.

[41] You might think this rather *illogical*, seeing that this whole subject is about the end states, not the route to them.

In principle, we are ready now to apply the scheme for calculating thermodynamic equilibria worked out in §9.2 to various specific cases: the classical monatomic ideal gas (§11), diatomic gases, magnetic systems, etc. (Part IV). But before we can in good faith embark on these practical calculations, we must deal with some conceptual issues:
— conditions for thermodynamic equilibrium (which, in our new language, means the state of maximum entropy subject to measurable constraints),
— its stability (if $dS_G = 0$, how do we know that it is a maximum, rather than a minimum?),
— 2-nd Law,
— the meaning of probabilities, information, its loss etc.
The first two of these are more mundane and will be dealt with in §10; the last two are rather tricky and are postponed to the "postscript" sections §§12 and 13.

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**Exercise 9.1. Elastic Chain.** A very simplistic model of an elastic chain is illustrated in Fig. 20. This is a 1D chain consisting of $N$ segments, each of which can be in one of two (non-degenerate) states: horizontal (along the chain) or vertical. Let the length of the segment be $a$ when it is horizontal and 0 when it is vertical. Let the chain be under fixed tension $\gamma$ and so let the energy of each segment be 0 when it is horizontal and $\gamma a$ when it is vertical. The temperature of the chain is $T$.

(a) What are the microstates of the chain? Using the canonical ensemble, work out the single-segment partition function and hence the partition function of the entire chain.

(b) *Entropic force.* Work out the relationship between mean energy $U$ and mean length $L$ of the chain and hence calculate the mean length as a function of $\gamma$ and $T$. Under what approximation do we obtain *Hooke's law*

$$\boxed{\gamma = Ak_B T(L - L_0)}\,, \tag{9.38}$$

where $L_0$ and $A$ are constants? What is the physical meaning of $L_0$? Physically, why is the tension required to stretch the chain to the mean length $L$ greater when the temperature is higher?

(c) Calculate the heat capacity for this chain and sketch it as a function of temperature (pay attention to what quantity is held constant for the calculation of the heat capacity). Why physically does the heat capacity vanish both at small and large temperatures?

(d) *Negative temperature.* If you treat the mean energy $U$ of the chain as given and temperature as the quantity to be found, you will find that temperature can be negative! Sketch $T$ as a function of $U$ and determine under what conditions $T < 0$. Why is this possible in this system and not, say, for the ideal gas? Why does the stability argument from §10.5.2 not apply here?

(e) *Superfluous constraints.* This example illustrates that if you have more measurements and so more constraints, you do not necessarily get different statistical mechanics (so the maximum-entropy principle is less subjective than it might seem to be; see §12.3).

So far we have treated our chain as a canonical ensemble, i.e., we assumed that the only constraint on probabilities would be the mean energy $U$. Suppose now that we have both a thermometer and a ruler and so wish to maximise entropy subject to two constraints: the mean energy is $U$ and the mean length of the chain is $L$. Do this and find the probabilities of the microstates $\alpha$ of the chain as functions of their energies $E_\alpha$ and corresponding chain lengths $\ell_\alpha$. Show that the maximisation problem only has a solution when $U$ and $L$ are in a specific relationship with each other—so the new constraint is not independent and does not bring in any new physics. Show that in this case one of the Lagrange multipliers is arbitrary (and so can be set to 0—e.g., the one corresponding to the constraint of fixed $L$; this constraint is superfluous so we are back to the canonical ensemble).

(f) It is obviously a limitation of our model that the energy and the length of the chain are in one-to-one correspondence: thus, you would not be able to construct from this model the standard thermodynamics based on tension force and chain length, with the latter changeable independently from the energy. Invent your own model in which $U$ and $L$ can be varied independently and work out its statistical mechanics (partition function) and its thermodynamics (entropy,

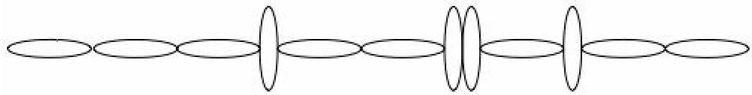

FIGURE 20. A model of elastic chain (Exercise 9.1).

energy, heat capacity, Hooke's law, etc.).[42] One possibility might be to allow the segments to have more than two states, with some states having the same energy but contributing to the total length in a different way (or vice versa), e.g., to enable the segments to fold back onto each other.

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The tension force (9.38) is an example of an *entropic force*. To be precise, the entropic force is the equal and oppositely directed counterforce with which the elastic chain responds to an externally applied force of magnitude $\gamma$ required to keep the chain at mean length $L$. There is no fundamental interaction associated with this force[43]—indeed this force only exists if temperature is non-zero and results from the statistical tendency for the chain to maximise its entropy, so the segments of the chain cannot all be in the horizontal state and the chain wants to shrink if stretched beyond its natural tension-free equilibrium length (which is $Na/2$). In the currently very fashionable language, such a force is called *emergent*, being a member of the class of *emergent phenomena*, i.e., phenomena that result from collective behaviour of many simple entities embedded in an environment (e.g., a heat bath setting $T$; see §10.3) but have no fundamental prototype in the individual physics of these simple entities.

Relatively recently, Verlinde (2011) made a splash by proposing that gravity was not a fundamental force but an emergent entropic one, somewhat analogous to our $\gamma = -T\partial S/\partial L$, but with entropy measuring (in a certain rather ingenious way) the information associated with positions of material bodies in space.

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**Exercise 9.2. Elastic Chain with Interactions.** In pursuit of a model with energy not hard-coupled to length (Exercise 9.1f), one of my students (Radek Grabarczyk, 2020) proposed an elastic chain in which there is an additional energy cost (below denoted $J$) associated with with two neighbouring links being in different states. Namely, let the microstates of the chain be determined by the states of the links, $\alpha = \{s_1, \dots, s_N\}$, where $s_i = 0$ or 1 for horizontal or vertical links, respectively, and the energy of this state to be

$$E_\alpha = \varepsilon \sum_{i=1}^{N} s_i + J \sum_{i=1}^{N} (s_i - s_{i+1})^2, \tag{9.39}$$

where $\varepsilon = \gamma a$ and, for future computational simplicity, we assume the chain to be periodic, i.e., $s_{N+1} = s_1$. This is an example of a statistical-mechanical system with interactions. The erudites amongst you might realise that this is exactly equivalent to the *1D Ising Model*—I leave it as an exercise to those erudites to work out the change of variables that turns (9.39) into the standard expression for the Ising Hamiltonian. This is, however, not necessary for being able to do what is asked for below.

(a) *Partition function.* Show that the partition function for this system can be written as

$$Z(\beta) = \mathrm{Tr}\big(\mathbf{A}^N\big), \tag{9.40}$$

where the $2 \times 2$ matrix $\mathbf{A}$ (called *transfer matrix*) has elements

$$A_{ss'} = e^{-\beta\varepsilon s/2} e^{-\beta J (s-s')^2} e^{-\beta\varepsilon s'/2} \quad \Rightarrow \quad \mathbf{A} = \begin{bmatrix} 1 & e^{-\beta(J+\varepsilon/2)} \\ e^{-\beta(J+\varepsilon/2)} & e^{-\beta\varepsilon} \end{bmatrix}. \tag{9.41}$$

---

[42]Exercise 14.7 is the $PV$ analog of this calculation.

[43]In our model, on the microscopic level, it *costs* $\gamma a$ amount of energy to put a link into the vertical state, thus shortening the chain. Nevertheless, a chain of $N$ links in contact with a thermal bath will resist stretching!

Hence show that, for $N \gg 1$,

$$Z(\beta) = \left[\frac{1+e^{-\beta\varepsilon}}{2} + \sqrt{\left(\frac{1+e^{-\beta\varepsilon}}{2}\right)^2 - e^{-\beta\varepsilon}\left(1-e^{-\beta J}\right)}\right]^N. \tag{9.42}$$

(b) Work out the thermodynamics of this chain. Interesting dependence of $L$ (length) on $\gamma$ (tension) can be found for the case $J < 0$ (i.e., when neighbouring links are energetically encouraged to be in different states).

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## 10. Thermodynamic Equilibria and Stability

Much of the discussion here will be about systems with different equilibrium characteristics being put in contact with each other and arriving at a new equilibrium.

### 10.1. *Additivity of Entropy*

Consider two systems:

System 1: microstates $\alpha$, energy levels $E_\alpha^{(1)}$, probabilities $p_\alpha^{(1)}$,
System 2: microstates $\alpha'$, energy levels $E_{\alpha'}^{(2)}$, probabilities $p_{\alpha'}^{(2)}$,

Now put them together into a composite system, but in such a way that the two constituent systems are in *"loose" thermal contact*, meaning that the microstates of the two systems are independent.[44] Then the microstates of the composite system are

$(\alpha, \alpha')$ with energy levels $E_{\alpha\alpha'} = E_\alpha^{(1)} + E_{\alpha'}^{(2)}$, probabilities $p_{\alpha\alpha'} = p_\alpha^{(1)} \cdot p_{\alpha'}^{(2)}$.

The Gibbs entropy of this system is

$$\begin{aligned} S_{\rm G} &= -\sum_{\alpha\alpha'} p_{\alpha\alpha'} \ln p_{\alpha\alpha'} = -\sum_{\alpha\alpha'} p_\alpha^{(1)} p_{\alpha'}^{(2)} \ln\left(p_\alpha^{(1)} p_{\alpha'}^{(2)}\right) \\ &= -\sum_\alpha p_\alpha^{(1)} \ln p_\alpha^{(1)} \underbrace{\sum_{\alpha'} p_{\alpha'}^{(2)}}_{=1} - \sum_{\alpha'} p_{\alpha'}^{(2)} \ln p_{\alpha'}^{(2)} \underbrace{\sum_\alpha p_\alpha^{(1)}}_{=1} = S_{{\rm G},1} + S_{{\rm G},2}. \end{aligned} \tag{10.1}$$

Thus, *Gibbs entropy is additive.*[45] So is, of course, mean energy:

$$U = \sum_{\alpha\alpha'} E_{\alpha\alpha'} p_{\alpha\alpha'} = \sum_\alpha E_\alpha^{(1)} p_\alpha^{(1)} \underbrace{\sum_{\alpha'} p_{\alpha'}^{(2)}}_{=1} + \sum_{\alpha'} E_{\alpha'}^{(2)} p_{\alpha'}^{(2)} \underbrace{\sum_\alpha p_\alpha^{(1)}}_{=1} = U_1 + U_2. \tag{10.2}$$

In equilibrium, the Gibbs entropy is the same as the thermodynamical entropy, $k_{\rm B} S_{\rm G} = S$ [see (9.14)], so

$$S = S_1 + S_2. \tag{10.3}$$

---

Note that in fact, in equilibrium, everything can be derived from the additivity of the energy

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[44]In the language of Quantum Mechanics, the eigenstates of a composite system are products of the eigenstates of its (two) parts. This works, e.g., for gases or fluids, but not for solids, where states are fully collective. You will find further discussion of this in Binney & Skinner (2013), §6.1.

[45]Note that if in constructing the expression for entropy we followed the formal route offered by Shannon's Theorem (§8.1.5), this would be guaranteed automatically (requirement 5 imposed on $S_{\rm G}$ in §8.1.5).

levels: indeed, $E_{\alpha\alpha'} = E^{(1)}_\alpha + E^{(2)}_{\alpha'}$ implies that *partition functions multiply:* for a composite system at a single temperature (otherwise it would not be in equilibrium; see §10.2),

$$Z(\beta) = \sum_{\alpha\alpha'} e^{-\beta E_{\alpha\alpha'}} = \sum_{\alpha\alpha'} e^{-\beta\left[E^{(1)}_\alpha + E^{(2)}_{\alpha'}\right]} = \left(\sum_\alpha e^{-\beta E^{(1)}_\alpha}\right)\left(\sum_{\alpha'} e^{-\beta E^{(2)}_{\alpha'}}\right) = Z_1(\beta)Z_2(\beta). \tag{10.4}$$

Therefore, the canonical equilibrium probabilities are

$$p_{\alpha\alpha'} = \frac{e^{-\beta E_{\alpha\alpha'}}}{Z} = \frac{e^{-\beta E^{(1)}_\alpha}}{Z_1}\frac{e^{-\beta E^{(2)}_{\alpha'}}}{Z_2} = p^{(1)}_\alpha p^{(2)}_{\alpha'} \tag{10.5}$$

and also

$$F = -k_\mathrm{B}T\ln Z = -k_\mathrm{B}T\ln(Z_1Z_2) = F_1 + F_2, \tag{10.6}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial F_1}{\partial T}\right)_V - \left(\frac{\partial F_2}{\partial T}\right)_V = S_1 + S_2, \tag{10.7}$$

$$U = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial\ln(Z_1Z_2)}{\partial\beta} = U_1 + U_2. \tag{10.8}$$

---

## 10.2. *Thermal Equilibrium*

We can now derive some consequences of the additivity of entropy coupled with the principle of obtaining the equilibrium state by maximising it.

Consider putting two systems (each in its own equilibrium) into loose thermal contact, but otherwise keeping them isolated (to be precise, we let them exchange energy with each other but not with anything else). Then, to find the new equilibrium, we must keep the total energy constant and maximise entropy:

$$U = U_1 + U_2 = \text{const} \tag{10.9}$$

(because energy levels add) and

$$S = S_1 + S_2 \to \max \tag{10.10}$$

(because we have created a composite system, as in §10.1). These conditions are implemented by setting the differentials of both the total energy and the total entropy to zero while allowing changes in the energies and entropies of the two sub-systems:

$$\mathrm{d}U = \mathrm{d}U_1 + \mathrm{d}U_2 = 0 \quad\Rightarrow\quad \mathrm{d}U_2 = -\mathrm{d}U_1, \tag{10.11}$$

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 = \frac{\partial S_1}{\partial U_1}\,\mathrm{d}U_1 + \frac{\partial S_2}{\partial U_2}\,\mathrm{d}U_2 = \left(\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right)\mathrm{d}U_1 = 0. \tag{10.12}$$

From the fundamental equation of thermodynamics (9.15),[46]

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{P}{T}\,\mathrm{d}V, \tag{10.13}$$

we get

$$\frac{1}{T} = \frac{\partial S}{\partial U}, \tag{10.14}$$

so (10.12) is

$$\mathrm{d}S = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\mathrm{d}U_1 = 0 \quad\Rightarrow\quad \boxed{T_1 = T_2}\,. \tag{10.15}$$

[46] This equation is only valid for equilibrium states, so its use here means that we are assuming the two subsystems and their composite all to be in equilibrium at the beginning and at the end of this experiment.

Thus, *in equilibrium, two systems in loose thermal contact will have equal temperatures.* This is called *thermal equilibrium.*

Note also that, if initially $T_1 \neq T_2$, the direction of change is set by $\mathrm{d}S > 0$, so $T_1 < T_2 \Leftrightarrow \mathrm{d}U_1 > 0$, i.e., *energy flows from hot to cold.*

---

What we have done can be recast formally as a Lagrange multiplier calculation: we are maximising $S_1 + S_2$ subject to $U_1 + U_2 = U$, so, unconditionally,

$$S_1 + S_2 - \lambda(U_1 + U_2 - U) \to \max. \tag{10.16}$$

This gives

$$\left(\frac{\partial S_1}{\partial U_1} - \lambda\right) \mathrm{d}U_1 + \left(\frac{\partial S_2}{\partial U_2} - \lambda\right) \mathrm{d}U_2 + (U_1 + U_2 - U)\mathrm{d}\lambda = 0 \quad \Rightarrow \quad \frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2} = \lambda = \frac{1}{T}. \tag{10.17}$$

---

*NB:* The validity of (10.14) does *not* depend on the identification of $S$ and $T$ with the entropy and temperature from empirical thermodynamics, the equation holds for the statistical-mechanical entropy (measure of uncertainty in the distribution $\{p_\alpha\}$) and statistical-mechanical temperature (Lagrange multiplier associated with fixed mean energy in the canonical ensemble). The above argument therefore shows that *the statistical-mechanical temperature is a sensible definition of temperature*: it is a scalar function that is the same across a composite system in equilibrium. This property then allows one to introduce a *thermometer* based on this temperature and hence a *temperature scale* (recall that in Thermodynamics, temperature was introduced either via the 0-th Law, as just such a function, which, however, did not have to be unique, or as the universal integrating factor of $\mathrm{d}Q_{\mathrm{rev}}$—Kelvin's definition, which we used in §9.2 when proving the equivalence between thermodynamical and statistical-mechanical temperatures). I am stressing this to re-emphasise the point, made in §9.5, that Thermodynamics can be derived entirely from Statistical Mechanics.

## 10.3. *Physical Interpretation of the Canonical Ensemble*

This is an appropriate moment to discuss what the canonical distribution actually describes physically.

Recall that this distribution followed from stipulating that probabilities of the system's microstates should be maximally unbiased subject only to conspiring to give some fixed (measurable) value of the mean energy $U$. The resulting Gibbs distribution (9.8) depended on a single parameter $\beta$, which we now know is the inverse temperature of the system and which was calculated via the implicit equation (9.9),

$$U = -\frac{\partial \ln Z}{\partial \beta} \quad \Rightarrow \quad \beta = \frac{1}{k_{\mathrm{B}} T} = \beta(U, \dots). \tag{10.18}$$

But the structure of the theory that has emerged (*implicit* equation for $\beta$) and the experience (or anticipation) of the kinds of questions that we are likely to be interested in both suggest that, in fact, it is much preferable to think of the mean energy as a function of temperature, $U = U(T, \dots)$, with $T$ as an "input parameter." This is preferable because the temperature of a system is often known by virtue of the system being in contact with surroundings, a.k.a. *heat reservoir* or *heat bath*, whose temperature is fixed—usually because the system under consideration is small compared to the heat bath and so can draw from or give up to the latter arbitrary amounts of energy without affecting the temperature of the heat bath very much. In equilibrium, $T_{\mathrm{system}} = T_{\mathrm{bath}}$, as we proved in §10.2.

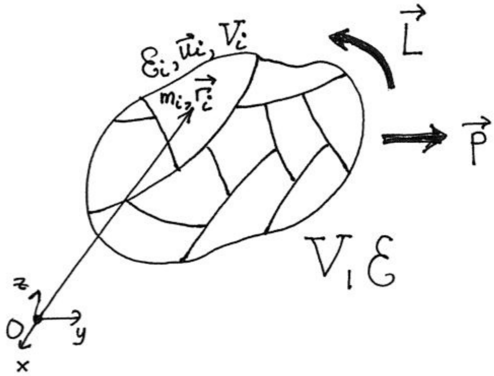


FIGURE 21. A composite system.

Thus, this is what *the canonical ensemble describes: microstates of a system in thermal contact with a heat bath at fixed temperature.*

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One can explicitly construct the Gibbs distribution on this basis if one starts from a (fictional) "closed system" with equal probabilities for all its microstates (the "microcanonical ensemble") and then considers a small part of it. This will be discussed in detail in §12.1.2 (or see, e.g., Blundell & Blundell 2009, §4.6, Landau & Lifshitz 1980, §28).

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*NB:* To make statistical inferences about the state of a system, you can maximise entropy subject to whatever constraints you like—but you are not necessarily guaranteed to get a useful result. If you want to get some sensible physics out, you have to choose your constraints judiciously. We now see that mean energy is indeed such a judicious choice for a system in a heat bath—this is not particularly surprising, since energy is what is exchanged when systems settle in thermal equilibrium. As we shall see in §10.4, it is generally a good strategy to use conserved quantities as constraints.

### 10.4. *Mechanical and Dynamical Equilibria*

[Literature: Landau & Lifshitz (1980), §§10, 12]

So far, we have focused on energy as the variable quantity exchangeable between systems (or between the system and the heat bath), while treating the volume of the system as a fixed external parameter and also assuming implicitly that the system was static (neither it nor its constituent parts had a velocity). Let us now generalise and consider some number of systems (Fig. 21), indexed by $i$, each having

total energy $\mathcal{E}_i$,
mass $m_i$,
velocity $\boldsymbol{u}_i$,
centre of mass position $\boldsymbol{r}_i$,
and volume $V_i$.

We now join them all together (in "loose contact," as explained in §10.1, so their microstates remain independent) and allow them to exchange energy, momentum, angular momentum and also to push on each other ("exchange volume," but not merge). The combined system will have some total energy, momentum, angular momentum and volume, which we expect to be able to measure. The equilibrium state of this system must be the state of maximum entropy subject to the following conservation laws:

$$\sum_i \mathcal{E}_i = \mathcal{E} \qquad \text{total energy,} \tag{10.19}$$

$$\sum_i m_i \boldsymbol{u}_i = \boldsymbol{p} \qquad \text{total momentum,} \tag{10.20}$$

$$\sum_i m_i \boldsymbol{r}_i \times \boldsymbol{u}_i = \boldsymbol{L} \qquad \text{total angular momentum,} \tag{10.21}$$

$$\sum_i V_i = V \qquad \text{total volume.} \tag{10.22}$$

Thus, we must maximise

$$\sum_i S_i - \lambda \left( \sum_i \mathcal{E}_i - \mathcal{E} \right) - \boldsymbol{a} \cdot \left( \sum_i m_i \boldsymbol{u}_i - \boldsymbol{p} \right) - \boldsymbol{b} \cdot \left( \sum_i m_i \boldsymbol{r}_i \times \boldsymbol{u}_i - \boldsymbol{L} \right) - \sigma \left( \sum_i V_i - V \right) \to \max, \tag{10.23}$$

where $\lambda$, $\boldsymbol{a}$, $\boldsymbol{b}$ and $\sigma$ are Lagrange multipliers. The variables with respect to which we must maximise this expression are $\{\mathcal{E}_i, \boldsymbol{u}_i, V_i\}$, $\lambda$, $\boldsymbol{a}$, $\boldsymbol{b}$, and $\sigma$ (it is understood that each sub-system is already in equilibrium, i.e., its entropy $S_i$ is already maximised for given values of its own parameters and observables, as in §10.2). The masses $\{m_i\}$ are not included in this set because we are assuming that our systems cannot exchange matter—we will see in §14 how to handle the possibility that they might.[47] We also do not include the positions $\{\boldsymbol{r}_i\}$ amongst the variables because the entropy $S_i$ cannot depend on where the system $i$ is—this is because $S_i$ depends only on the probabilities of the system's microstates $\{p_\alpha\}$, which clearly depend only on the internal workings of the system, not on its position in space (unless there is some inhomogeneous external potential in which this entire assemblage resides and which would then affect energy levels—I shall not consider this possibility until §14.5).

By the same token, the entropy of each subsystem can depend only on its *internal* energy, not on that of its macroscopic motion, because the probabilities $\{p_\alpha\}$ are, by Galilean invariance, the same in any inertial frame. The internal energy is

$$U_i = \mathcal{E}_i - \frac{m_i u_i^2}{2} \tag{10.24}$$

(because the *total* energy $\mathcal{E}_i$ consists of the internal one, $U_i$, and the kinetic energy of the system's macroscopic motion, $m_i u_i^2/2$). Therefore,

$$S_i = S_i(U_i, V_i) = S_i \left( \mathcal{E}_i - \frac{m_i u_i^2}{2}, V_i \right). \tag{10.25}$$

Thus, $S_i$ depends on both $\mathcal{E}_i$ and $\boldsymbol{u}_i$ via its internal-energy dependence.

*NB:* We treat $\{\mathcal{E}_i\}$, not $\{U_i\}$, as variables with respect to which we will be maximising entropy because only the total energy of the system is constrained by the energy-conservation law—it is perfectly fine for energy to be transferred between internal and kinetic as the system seeks equilibrium.

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[47] However, if we allowed such an exchange, we would have to disallow something else, for example exchange of volume—otherwise, how would we define where one system ends and another begins? Cf. Exercise 14.8.

Differentiating the expression (10.23) with respect to $\mathcal{E}_i$, $\boldsymbol{u}_i$ and $V_i$, and demanding that all these derivatives vanish, we find

$$\left(\frac{\partial S_i}{\partial \mathcal{E}_i}\right)_{\boldsymbol{u}_i,V_i} - \lambda = 0 \qquad \text{thermal equilibrium,} \tag{10.26}$$

$$\left(\frac{\partial S_i}{\partial \boldsymbol{u}_i}\right)_{\mathcal{E}_i,V_i} - m_i\left(\boldsymbol{a} + \boldsymbol{b}\times\boldsymbol{r}_i\right) = 0 \qquad \text{dynamical equilibrium,} \tag{10.27}$$

$$\left(\frac{\partial S_i}{\partial V_i}\right)_{\mathcal{E}_i,\boldsymbol{u}_i} - \sigma = 0 \qquad \text{mechanical equilibrium.} \tag{10.28}$$

10.4.1. *Thermal Equilibrium*

Using again (10.14), we find that (10.26) tells us that in equilibrium, the temperatures of all subsystems must be equal to the same Lagrange multiplier and, therefore, to each other:

$$\left(\frac{\partial S_i}{\partial \mathcal{E}_i}\right)_{\boldsymbol{u}_i,V_i} = \left(\frac{\partial S_i}{\partial U_i}\right)_{V_i} = \frac{1}{T_i} \quad \Rightarrow \quad \boxed{T_i = \frac{1}{\lambda} \equiv T}\,. \tag{10.29}$$

This is simply the generalisation to more than two subsystems of the result already obtained in §10.2.

10.4.2. *Mechanical Equilibrium*

Going back to the fundamental equation of thermodynamics (10.13), we note that

$$\left(\frac{\partial S_i}{\partial V_i}\right)_{\mathcal{E}_i,\boldsymbol{u}_i} = \left(\frac{\partial S_i}{\partial V_i}\right)_{U_i} = \frac{P_i}{T_i}. \tag{10.30}$$

But we already know that all $T_i = T$, so (10.28) implies that in equilibrium, all pressures are equal as well:

$$\boxed{P_i = \sigma T \equiv P} \tag{10.31}$$

(note that for ideal gas, this Lagrange multiplier is particle density: $\sigma = nk_{\rm B}$; cf. Exercise 14.7). Physically, this says that in equilibrium, everything is in *pressure balance* (otherwise volumes will expand or shrink to make it so).

10.4.3. *Dynamical Equilibrium*

Finally, let us work out what (10.27) means. In view of (10.25) and (10.29),

$$\left(\frac{\partial S_i}{\partial \boldsymbol{u}_i}\right)_{\mathcal{E}_i,V_i} = -m_i\boldsymbol{u}_i\left(\frac{\partial S_i}{\partial U_i}\right)_{V_i} = -\frac{m_i\boldsymbol{u}_i}{T_i} = -\frac{m_i\boldsymbol{u}_i}{T}. \tag{10.32}$$

Then, from (10.27),

$$\boxed{\boldsymbol{u}_i = -T\boldsymbol{a} - T\boldsymbol{b}\times\boldsymbol{r}_i \equiv \boldsymbol{u} + \boldsymbol{\Omega}\times\boldsymbol{r}_i}\,, \tag{10.33}$$

where we have defined $\boldsymbol{u} \equiv -T\boldsymbol{a}$ and $\boldsymbol{\Omega} \equiv -T\boldsymbol{b}$. This means that *the only macroscopic motion that is possible in a system in equilibrium is an overall constant motion of the whole system in some direction plus a rigid-body rotation of the whole system.*

The main implication of these results is that *in a system in equilibrium, there cannot be any temperature or pressure gradients or any internal macroscopic motions (velocity gradients).* Statistical Mechanics does not tell us how this is achieved, but we know from our experience with Kinetic Theory that temperature and velocity gradients will relax to global equilibrium via thermal diffusivity and viscosity, respectively (see §§5–6).

A few further observations are in order.

1) In practice, mechanical equilibrium (pressure balance) is often achieved faster than the thermal and dynamical ones are: pressure imbalances will create uncompensated macroscopic forces, which will give rise to macroscopic motions, which will iron out pressure differences on dynamical time scales (recall the discussion of this topic at the end of §6.4.2).

2) All the arguments above are generalised in an obvious way to non-$PV$ systems.

3) Another type of equilibrium that we might have considered is *particle equilibrium*—by allowing our subsystems to exchange particles, subject to the overall conservation of their total number. This leads to the equalisation of the *chemical potential* across all subsystems—another Lagrange multiplier, which will be introduced in §14, when we study "open systems." Yet further generalisation will be to *phase* and *chemical equilibria*, discussed in §15.

4) In considering quantities other than energy as measurable constraints (momentum, angular, momentum, volume), we went beyond the canonical ensemble—and indeed, other ensembles can be constructed to handle situations where, besides energy, other quantities are considered known: e.g., mean angular momentum ("rotational ensemble", also due to Gibbs 1902), mean volume ("pressure ensemble"; see Exercise 14.7), mean particle number ("grand canonical ensemble"; see §14), etc. There is no ensemble based on the momentum of translational motion: indeed, if we consider non-rotating systems, (10.33) says that $\boldsymbol{u}_i = \boldsymbol{u}$ and we can always go to the frame of reference in which $\boldsymbol{u} = 0$ and the system is at rest.

## 10.5. *Stability*

How do we know that when we extremised $S$, the solution that we found was a maximum, not a minimum (or a saddle point)? This is equivalent to asking whether the equilibria that we found were *stable.* To check for stability, we need to calculate second derivatives of the entropy.

### 10.5.1. *Thermal Stability*

From (10.26) and (10.29),

$$\frac{\partial^2 S_i}{\partial \mathcal{E}_i^2} = \frac{\partial}{\partial \mathcal{E}_i}\frac{1}{T} = -\frac{1}{T^2}\frac{\partial T}{\partial \mathcal{E}_i} = -\frac{1}{T^2 C_{Vi}} < 0 \tag{10.34}$$

is a necessary condition for stability. Here

$$\frac{\partial \mathcal{E}_i}{\partial T} = \frac{\partial U_i}{\partial T} = C_{Vi} \tag{10.35}$$

is the heat capacity and so, in physics language, the inequality (10.34) is the requirement that the heat capacity should always be positive:

$$\boxed{C_V > 0}\,. \tag{10.36}$$

That this is always so can actually be proven directly by calculating $C_V = \partial U/\partial T$ from $U = -\partial \ln Z/\partial\beta$ and using the explicit Gibbs formula for $Z$.

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**Exercise 10.1. Heat Capacity from Canonical Ensemble.** Prove the inequality (10.36) by showing that

$$C_V = \frac{\langle \Delta E^2\rangle}{k_{\mathrm{B}} T^2}, \tag{10.37}$$

where $\langle \Delta E^2 \rangle$ is the mean square fluctuation of the system's energy around its mean energy $U$.

---

A curious example of the failure of thermal stability is the *thermodynamics of black holes*. A classical Schwarzschild black hole of mass $M$ has energy $U = Mc^2$ and a horizon whose radius is $R = 2GM/c^2$ and area is

$$A = 4\pi R^2 = \frac{16\pi G^2 M^2}{c^4}. \tag{10.38}$$

Hawking famously showed that such a black hole would emit radiation as if it were a black body (see §19) with temperature

$$T = \frac{\hbar c^3}{8\pi k_B G M}. \tag{10.39}$$

If we take all this on faith and integrate $\mathrm{d}S/\mathrm{d}U = 1/T$, the entropy of a black hole turns out to be proportional to the area of its horizon:

$$S = \frac{4\pi k_B G M^2}{\hbar c} = k_B \frac{A}{4\ell_P^2}, \quad \ell_P = \sqrt{\frac{G\hbar}{c^3}}, \tag{10.40}$$

where $\ell_P$ is the Planck length. This entropy accounts for the disappearance of the entropy of objects that fall into the black hole (or indeed of any knowledge that we might have of them), thus preventing violation of the second law of thermodynamics—even in the absence of Hawking's result, this would be reasonable grounds for expecting black holes to have entropy; indeed, long before Hawking discovered his radiation, Bekenstein (1973) had argued that this entropy should be proportional to the area of the horizon.

From (10.39) and (10.40), it follows that if $M$ is increased, $T$ goes down while $S$ goes up and so the heat capacity is negative. This can be interpreted to mean that a black hole is not really in equilibrium (indeed, we know that it evaporates, even if slowly) and that a population of black holes is an unstable system: they would merge with each other, producing ever larger but "colder" black holes.

How to construct the statistical mechanics of a black hole remains an active research question because we do not really know what the "microstates" are [although string theorists do have models of these microstates from which they are able to calculate $S$ and recover (10.40)]. I like and, therefore, recommend the paper by Gour (1999), where, with certain rather simple assumptions about these microstates, the black hole is treated via the maximum-entropy principle starting from the expectation of an observer being able to measure separately the black hole's mass and the area of its horizon (you can also follow the paper trail from there to various alternative schemes). Exercise 14.9 is a somewhat vulgarised version of this paper.

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10.5.2. *Dynamical Stability*

For simplicity, let us only consider the case with fixed volume and no rotation ($\boldsymbol{\Omega} = 0$). Then, denoting the vector components of the velocity $\boldsymbol{u}_i$ by Greek superscripts and using again the fact that $S_i$ is a function of $\boldsymbol{u}_i$ via its internal-energy dependence [see (10.25)], we find another necessary condition for stability:

$$\frac{\partial^2 S_i}{\partial u_i^\mu \partial u_i^\nu} = \frac{\partial}{\partial u_i^\mu}\left(-m_i u_i^\nu \frac{\partial S_i}{\partial U_i}\right) = -m_i \frac{\partial S_i}{\partial U_i}\,\delta_{\mu\nu} - m_i u_i^\nu \frac{\partial}{\partial u_i^\mu}\frac{\partial S_i}{\partial U_i}$$
$$= -\frac{m_i}{T}\delta_{\mu\nu} + \cancel{m_i^2 u_i^\mu u_i^\nu \frac{\partial^2 S_i}{\partial U_i^2}} < 0. \tag{10.41}$$

The second term can be eliminated because in equilibrium all velocities are the same $\boldsymbol{u}_i = \boldsymbol{u}$ and we can always go to the frame where $\boldsymbol{u} = 0$. The condition (10.41) is equivalent to

$$\boxed{T > 0}\,. \tag{10.42}$$

Thus, we have proven that *temperature must be positive*! Systems with negative temperature are unstable.

Another, more qualitative way of arguing this is as follows. The entropy of the composite system is

$$S = \sum_i S_i(U_i) = \sum_i S_i\left(\mathcal{E}_i - \frac{m_i u_i^2}{2}\right). \tag{10.43}$$

If temperature were negative,

$$\left(\frac{\partial S_i}{\partial U_i}\right)_{V_i} = \frac{1}{T} < 0, \tag{10.44}$$

then all $S_i$'s would be maximised by decreasing their argument as much as possible, i.e., by increasing all $u_i$'s subject to $\sum_i m_i \boldsymbol{u}_i = 0$. This means that all the parts of the system would fly in opposite directions (the system would blow up).

*NB:* The prohibition on negative temperatures can be relaxed if bits of the system are not allowed to move and/or if the system's allowed range of energies is bounded (see Exercise 9.1).[48]

A similar argument can be made for the *positivity of pressure:* if pressure is negative,

$$P_i = T\left(\frac{\partial S_i}{\partial V_i}\right)_{U_i} < 0, \tag{10.45}$$

then entropy in a (closed) system can increase if volume goes down, i.e., the system will shrink to nothing. In contrast, if $P > 0$, then entropy increases as $V$ increases (system expands)—but this is checked by walls or whatever external circumstances maintain the fixed total volume. This argument militates strongly against negative pressures, but it is not, in fact, completely prohibitive: negative pressures can exist (although usually in metastable states, to be discussed in Part VII)—this happens, for example, when cavities form or substances separate from walls, etc.

## 11. Statistical Mechanics of Classical Monatomic Ideal Gas

We are now going to go through our first example of a statistical mechanical calculation where we start with energy levels for a system, work out $Z$ and, therefore, $F$, then obtain from it the equation of state, energy and entropy as functions of temperature and volume, hence heat capacities etc.

We shall do this for a familiar system—*classical monatomic ideal gas*, for which we already know all the answers, obtained in §2 from a bespoke theory. Obtaining them again in a new way will help us convince ourselves of the soundness of the much more general formalism that we now have.

Our first objective is to calculate

$$\boxed{Z = \sum_\alpha e^{-\beta E_\alpha}}\,, \tag{11.1}$$

where $\{E_\alpha\}$ are the energy levels of our gas—i.e., of $N$ non-interacting particles in a box of volume $V$—corresponding to all possible states $\{\alpha\}$ in which these particles can

[48]Note, however, a recent objection to the idea of negative temperatures: Dunkel & Hilbert (2014). This paper also has all the relevant references on the subject; note that what they call "Gibbs entropy" is not the same thing as our Gibbs–Shannon entropy. If you are going to explore this literature, you may want to read §§12 and 13 first.

*collectively* find themselves. Thus, in order to compute $Z$, we must start by working out what are $\{\alpha\}$ and $\{E_\alpha\}$.

### 11.1. *Single-Particle States*

We do know what the possible states and energies are for a single particle: each of its states is characterised by its momentum $\boldsymbol{p}$ and the corresponding energy is

$$\varepsilon_{\boldsymbol{p}} = \frac{p^2}{2m}, \tag{11.2}$$

where $m$ is the particle's mass. Classically, we might be tempted to say that the states are characterised also by the particle's position $\boldsymbol{r}$, but we know from Quantum Mechanics that we cannot know both $\boldsymbol{p}$ and $\boldsymbol{r}$ exactly. As we are considering our particle to reside in a homogeneous box, the momentum is fixed and the particle can be anywhere—in fact, "the particle" is a *monochromatic wave* with wave number $\boldsymbol{k} = \boldsymbol{p}/\hbar$; if the box in which it lives has dimensions $L_x \times L_y \times L_z$, the wave numbers are quantised so that an integer number of periods can fit into the box:[49]

$$\boldsymbol{k} = \left(\frac{2\pi}{L_x}\,i_x, \frac{2\pi}{L_y}\,i_y, \frac{2\pi}{L_z}\,i_z\right), \tag{11.3}$$

where $(i_x, i_y, i_z)$ are integers. These triplets define a countably infinite number of single-particle states. The corresponding energy levels are

$$\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m}. \tag{11.4}$$

### 11.2. *Down the Garden Path...*

We have $N$ such particles in our box. Since they are non-interacting, you might think, **naïvely**, that this is a case of a composite system containing $N$ subsystems, each with microstates (11.3) and energy levels (11.4). If this were the case, then the collective microstates and energies of the gas in a box would be

$$\alpha = \{\boldsymbol{k}_1, \dots, \boldsymbol{k}_N\} \quad \Rightarrow \quad E_\alpha = \sum_{i=1}^{N} \varepsilon_{\boldsymbol{k}_i}. \tag{11.5}$$

This counting scheme will turn out to be **very wrong**, but let us explore where it leads—we will learn some useful things and later fix it without much extra work.

Under this scheme, the partition function is

$$Z = \sum_{\{\boldsymbol{k}_1,\dots,\boldsymbol{k}_N\}} e^{-\beta(\varepsilon_{\boldsymbol{k}_1} + \dots + \varepsilon_{\boldsymbol{k}_N})} = \Bigg[\underbrace{\sum_{\boldsymbol{k}} e^{-\beta\varepsilon_{\boldsymbol{k}}}}_{=Z_1}\Bigg]^N = Z_1^N, \tag{11.6}$$

where $Z_1$ is the *single-particle partition function*. So, if we can calculate $Z_1$, we are done.

[49]This works either if we consider the box to have reflecting boundary conditions and so require all our particles to be standing waves (see, e.g., Blundell & Blundell 2009, §21.1) or, even more straightforwardly, albeit less intuitively, if we use periodic boundary conditions.

11.3. *Single-Particle Partition Function*

We do this calculation by approximating $\sum_{\boldsymbol{k}}$ with an integral:

$$Z_1 = \sum_{\boldsymbol{k}} e^{-\beta\varepsilon_{\boldsymbol{k}}} = \sum_{\boldsymbol{k}} \underbrace{\frac{L_x L_y L_z}{(2\pi)^3}}_{\frac{V}{(2\pi)^3}} \underbrace{\frac{2\pi}{L_x}}_{\Delta k_x} \underbrace{\frac{2\pi}{L_y}}_{\Delta k_y} \underbrace{\frac{2\pi}{L_z}}_{\Delta k_z} e^{-\beta\varepsilon_{\boldsymbol{k}}} \approx \frac{V}{(2\pi)^3} \int \mathrm{d}^3\boldsymbol{k}\, e^{-\beta\hbar^2 k^2/2m}, \quad (11.7)$$

where $\Delta k_{x,y,z} = 2\pi/L_{x,y,z}$ are the spacings between discrete points in the "grid" in $\boldsymbol{k}$ space [see (11.3)]. The continuous approximation is good as long as the typical scale of variation of $k$ in the integrand is much larger than the $\boldsymbol{k}$-grid spacing:

$$k \sim \sqrt{\frac{2m}{\beta\hbar^2}} = \frac{\sqrt{2mk_\mathrm{B}T}}{\hbar} \gg \Delta k_{x,y,z} = \frac{2\pi}{L_{x,y,z}} \sim \frac{2\pi}{V^{1/3}}$$

$$\Leftrightarrow \quad T \gg \frac{\hbar^2}{mk_\mathrm{B}V^{2/3}} = \frac{\hbar^2}{mk_\mathrm{B}}\left(\frac{n}{N}\right)^{2/3} = \frac{T_\mathrm{deg}}{N^{2/3}}, \quad (11.8)$$

where $T_\mathrm{deg}$ is the degeneration temperature—the lower limit to the temperatures at which the classical approximation can be used, given by (2.29). The condition (11.8) is easily satisfied, of course, because $N \gg 1$.

The triple Gaussian integral in (11.7) is instantly calculable:

$$Z_1 = \frac{V}{(2\pi)^3}\left(\int \mathrm{d}k_x\, e^{-\beta\hbar^2 k_x^2/2m}\right)^3 = \frac{V}{(2\pi)^3}\left(\frac{2m}{\beta\hbar^2}\,\pi\right)^{3/2} = \frac{V}{\hbar^3}\left(\frac{mk_\mathrm{B}T}{2\pi}\right)^{3/2} \equiv \frac{V}{\lambda_\mathrm{th}^3}, \quad (11.9)$$

where we have introduced the *thermal wavelength*

$$\lambda_\mathrm{th} = \hbar\sqrt{\frac{2\pi}{mk_\mathrm{B}T}}, \quad (11.10)$$

a quantity that is obviously (dimensionally) convenient here, will continue to prove convenient further on, and acquire a modicum of physical meaning in (11.31).

---

11.4. *Digression: Density of States*

When we calculate partition functions based on the canonical distribution, only microstates with different energies give different contributions to the sum over states [see (11.1)], whereas microstates whose energies are the same ("degenerate" energy levels) all have the same probabilities and so contribute similarly. Therefore, we can write $Z$ as a weighted integral over energies or over some variable that is in one-to-one correspondence with energy—in the case of energy levels of the ideal gas, $k = |\boldsymbol{k}|$ [see (11.4)]. In this context, there arises the quantity called the *density of states*—the number of microstates per $k$, or per $\varepsilon$.

For the classical monatomic ideal gas, we can determine this quantity by transforming the integration in (11.7) to polar coordinates and integrating out the angles in $\boldsymbol{k}$ space:

$$Z_1 = \frac{V}{(2\pi)^3}\int_0^\infty \mathrm{d}k\, 4\pi k^2\, e^{-\beta\hbar^2k^2/2m} \equiv \int_0^\infty \mathrm{d}k\, g(k)\, e^{-\beta\hbar^2k^2/2m}, \quad g(k) = \frac{Vk^2}{2\pi^2}, \quad (11.11)$$

where $g(k)$ is the density of states (per $k$). The fact that $g(k)$ grows with $k$ says that energy levels are increasingly more degenerate as $k$ goes up (the number of states in a spherical shell of width $\mathrm{d}k$ in $\boldsymbol{k}$ space, $g(k)\mathrm{d}k$, goes up).

Similarly, transforming the integration variable in (11.11) to $\varepsilon = \hbar^2k^2/2m$, we can write

$$Z_1 = \int_0^\infty \mathrm{d}\varepsilon\, g(\varepsilon)\, e^{-\beta\varepsilon}, \quad g(\varepsilon) = \frac{2}{\sqrt{\pi}}\frac{V}{\lambda_\mathrm{th}^3}\frac{\sqrt{\varepsilon}}{(k_\mathrm{B}T)^{3/2}}, \quad (11.12)$$

where $g(\varepsilon)$ is the density of states per $\varepsilon$ (*not* the same function as $g(k)$, despite, somewhat sloppily, being denoted by the same letter).

Note that the functional form of $g(k)$ or $g(\varepsilon)$ depends on the *dimension of space*.

---

**Exercise 11.1. Density of States in $d$ Dimensions.** (a) Calculate $g(k)$ and $g(\varepsilon)$ for a classical monatomic ideal gas in $d$ dimensions (also do the $d = 1$ and $d = 2$ cases separately and check that your general formula reduces to the right expressions in 1D, 2D and 3D).

(b) Do the same calculation for an ultrarelativistic (i.e., $\varepsilon \gg mc^2$) monatomic ideal gas.

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### 11.5. *Equipartition Theorem*

From (11.9), we can, via (9.9), calculate the mean energy of a single particle [cf. (2.23) and (11.34)]:

$$U_1 = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2} k_{\rm B}T, \tag{11.13}$$

which follows solely from the $\beta$ dependence of $Z_1$. This result can be generalised to an abstract system that has $d$ degrees of freedom $Q_1, \dots, Q_d$ and whose energy depends on them all quadratically:

$$\varepsilon_{\boldsymbol{Q}} = \sum_{i=1}^{d} a_i Q_i^2, \tag{11.14}$$

where $a_i$ are some constants. Then

$$Z = \sum_{Q_1} \cdots \sum_{Q_d} e^{-\beta\sum_i a_i Q_i^2} = \prod_{i=1}^{d} \sum_{Q_i} e^{-\beta a_i Q_i^2} = \prod_{i=1}^{d} \Delta Q_i \underbrace{\int \mathrm{d}Q_i e^{-\beta a_i Q_i^2}}_{=\sqrt{\pi/\beta a_i}} = \frac{\rm const}{\beta^{d/2}}, \tag{11.15}$$

whence

$$\boxed{U = \frac{d}{2} k_{\rm B}T}\,. \tag{11.16}$$

This is called *the equipartition theorem:* each quadratic degree of freedom adds $k_BT/2$ to the system's mean energy. A point particle with three translational degrees of freedom ($Q_1 = p_x$, $Q_2 = p_y$, $Q_3 = p_z$) has (11.13), but we now have a generic way of calculating both partition functions and mean energies for particles (or indeed multi-particle systems) that have other ways of storing energy, e.g., the rotating and vibrating dumbbells that model diatomic gases (see Part IV).

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### 11.6. *Disaster Strikes*

Using (11.6) and (11.9), we deduce the $N$-particle partition function and, therefore, the free energy:

$$Z = Z_1^N = \left(\frac{V}{\lambda_{\rm th}^3}\right)^N \quad \Rightarrow \quad F = -k_{\rm B}T\ln Z = -k_{\rm B}TN\ln\left(\frac{V}{\lambda_{\rm th}^3}\right). \tag{11.17}$$

Hence the entropy:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_{\rm B}N\ln\left(\frac{V}{\lambda_{\rm th}^3}\right) + \frac{3}{2}k_{\rm B}N = k_{\rm B}N\left[\ln N + \frac{3}{2} - \ln(n\lambda_{\rm th}^3)\right], \quad n = \frac{N}{V}. \tag{11.18}$$

The last expression for $S$ is a complete and unmitigated disaster because it is *not additive!!!* Indeed, suppose we double the amount of gas: $N \to 2N$, $V \to 2V$ (density $n$ stays constant), then

$$S_{\rm new} - 2S_{\rm old} = 2k_{\rm B}N\ln 2. \tag{11.19}$$

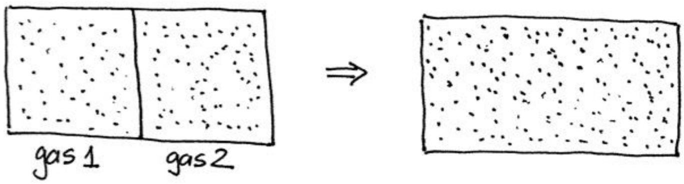


FIGURE 22. Gibbs Paradox.

This is obviously unacceptable as our entire theory was built on additivity of entropy (see §10 and, indeed, §8.1.5, where Gibbs–Shannon entropy is additive by definition).

So what went wrong?

### 11.7. *Gibbs Paradox*

To debug our calculation, it is useful to consider the following famous example.

Suppose we have two isolated chambers separated by a partition, one containing gas 1, the other gas 2, $N$ particles of each. Remove the partition and let the gases mix (Fig. 22). Each gas expands into vacuum (Joule expansion), so each picks up $k_B N \ln 2$ of entropy and so[50]

$$\Delta S = 2k_B N \ln 2. \tag{11.20}$$

This is certainly true if the two gases are *different*. If, on the other hand, the two gases are *the same*, surely we must have

$$\Delta S = 0, \tag{11.21}$$

because, if we reinserted the partition, we would be back to *status quo ante!* This inconsistency is called *the Gibbs Paradox*.

As often happens, realising there is a paradox helps resolve it.

### 11.8. *Distinguishability*

It is now clear where the problem came from: when we counted the states of the system (§11.2), we *distinguished* between individual particles: e.g., swapping momenta [$\boldsymbol{k}_i$ and $\boldsymbol{k}_j$, assuming $\boldsymbol{k}_i \neq \boldsymbol{k}_j$, in (11.5)] between two particles would give a different microstate in our accounting scheme. In the Gibbs set up in §11.7, we got the spurious entropy increase after mixing identical gases by moving "individual" particles from one chamber to another.

In a quantum world, this problem does not arise because particles are in fact *indistinguishable* (interchanging them amounts to permuting the arguments of some big symmetric wave-function amplitude). One way of explaining this intuitively is to say that distinguishing particles amounts to pointing at them: "this one" or "that one," i.e., identifying their positions. But since their momenta are definite, their positions are in fact completely undeterminable, by the uncertainty principle: they are just waves in a box![51]

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[50] Another way to derive this result is by arguing (pretending these are classical particles) that after the partition is removed, there is additional uncertainty for each particle as to whether it ends up in chamber 1 or in chamber 2. These outcomes have equal probabilities 1/2, so the additional entropy per particle is, as per (8.7), $\Delta S_1 = -k_B(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}) = k_B \ln 2$ and so, for $2N$ particles, we get (11.20).

[51] A formal way of defining indistinguishably of particles without invoking Quantum Mechanics is to stipulate that all realistically measurable physical quantities will remain the same under any permutation of the particles.

In Part IV, you will see that in systems where individual particles are distinguishable, they are often fixed in some spatial positions (e.g., magnetisable spins in a lattice).

Thus, the microstates of a gas in a box should be designated not by lists of momenta of individual particles [see (11.5)], but by

$$\alpha = \{n_{\boldsymbol{k}_1}, n_{\boldsymbol{k}_2}, n_{\boldsymbol{k}_3}, \dots\}, \quad \sum_{\boldsymbol{k}} n_{\boldsymbol{k}} = N, \tag{11.22}$$

where $n_{\boldsymbol{k}_i}$ are *occupation numbers* of the single-particle microstates: $n_{\boldsymbol{k}_1}$ particles with wave number $\boldsymbol{k}_1$, $n_{\boldsymbol{k}_2}$ particles with wave number $\boldsymbol{k}_2$, etc., up to the total of $N$ particles. The corresponding *collective* energy levels are

$$E_\alpha = \sum_{\boldsymbol{k}} n_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}}. \tag{11.23}$$

### 11.9. *Correct Partition Function*

With this new counting scheme, we conclude that the $N$-particle partition function really is

$$Z = \sum_{\{n_{\boldsymbol{k}}\}} e^{-\beta \sum_{\boldsymbol{k}} n_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}}}, \tag{11.24}$$

where the sum is over all possible sequences $\{n_{\boldsymbol{k}}\}$ of occupation numbers, subject to $\sum_{\boldsymbol{k}} n_{\boldsymbol{k}} = N$. Calculating this sum is a somewhat tricky combinatorial problem—we will solve it in §16.2, but for our current purposes, we can use a convenient shortcut.

Suppose we are allowed to neglect all those collective microstates in which more than one particle occupies the same single-particle microstate, i.e.,

$$\text{for any } \boldsymbol{k}, \ \ n_{\boldsymbol{k}} = 0 \text{ or } 1. \tag{11.25}$$

Then the correct, collective microstates (11.22) are the same as our old, wrong ones (11.5) ("particle 1 has wave number $\boldsymbol{k}_1$, particle 2 has wave number $\boldsymbol{k}_2$, etc."; cases where $\boldsymbol{k}_1$, $\boldsymbol{k}_2$, ... are not different are assumed to contribute negligibly to $\sum_\alpha$ in the partition function), except the order in which we list the particles ought not to matter. Thus, we must correct our previous formula (11.6) for $Z$ to eliminate the overcounting of the microstates in which the particles were simply permuted—as the particles are indistinguishable, these are in fact *not* different microstates. The necessary correction is, therefore,[52]

$$\boxed{Z = \frac{Z_1^N}{N!}}. \tag{11.26}$$

Using (11.9) in (11.26), we have for the classical monatomic ideal gas,

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda_{\rm th}^3}\right)^N, \quad \lambda_{\rm th} = \hbar\sqrt{\frac{2\pi}{mk_{\rm B}T}}. \tag{11.27}$$

It might not be immediately obvious why the validity of the corrected formula (11.26) is restricted to the case (11.25), but breaks down if there are non-negligibly many multiply occupied states. The reason is that our original counting scheme (11.5) distinguished between cases such as "particle 1 has wave number $\boldsymbol{k}_1$, particle 2 has wave number $\boldsymbol{k}_2$, ..." vs. "particle 1 has wave number $\boldsymbol{k}_2$, particle 2 has wave number $\boldsymbol{k}_1$, ..." when $\boldsymbol{k}_1 \neq \boldsymbol{k}_2$—this was wrong and is corrected by the $N!$ factor, which removes all permutations

[52]Our old formula, $Z = Z_1^N$, is still fine for systems consisting of distinguishable elementary units (cf. Exercise 9.1 or the magnetic systems in Part IV).

of the particles; however, the scheme (11.5) did *not* distinguish between such cases for $\boldsymbol{k}_1 = \boldsymbol{k}_2$ and so, if they were present in abundance, the factor $N!$ would overcorrect.

So, before we use the new formula (11.27) to calculate everything, let us assess how good the assumption (11.25) is. In order for it to hold, we need that

$$\begin{matrix}\text{the number of available} \\ \text{single-particle states}\end{matrix} \quad \gg \quad \begin{matrix}\text{the number of} \\ \text{particles } N.\end{matrix} \tag{11.28}$$

The single-particle partition function (11.9) gives a decent estimate of the former quantity because the typical energy of the system will be $\varepsilon_{\boldsymbol{k}} \sim k_{\rm B}T$ and the summand in

$$Z_1 = \sum_{\boldsymbol{k}} e^{-\varepsilon_{\boldsymbol{k}}/k_{\rm B}T} \tag{11.29}$$

stays order unity roughly up to this energy, so the sum is simply of order of the number of microstates in the interval $\varepsilon_{\boldsymbol{k}} \lesssim k_{\rm B}T$.[53] Then the condition (11.28) becomes

$$\frac{V}{\lambda_{\rm th}^3} \gg N \quad \Leftrightarrow \quad \boxed{n\lambda_{\rm th}^3 \ll 1}\,. \tag{11.30}$$

Another popular way of expressing this condition is by stating that the number density of the particles must be much smaller than the "quantum concentration" $n_{\rm Q}$:

$$n \ll n_{\rm Q} \equiv \frac{1}{\lambda_{\rm th}^3}. \tag{11.31}$$

Physically, the quantum concentration is the number of single-particle states per unit volume (this is meaningful because the number of states is an extensive quantity: in larger volumes, there are more wave numbers available, so there are more states).

The condition (11.31) is actually the condition for the *classical limit* to hold, $T \gg T_{\rm deg}$ [see (2.29)], guaranteeing the absence of quantum correlations (which have to do with precisely the situation that we wish to neglect: more than one particle trying to be in the same single-particle state; see Part VI). When $n \sim n_{\rm Q}$ or larger, we can no longer use (11.26) and are in the realm of *quantum gases*. Substituting the numbers, which, e.g., for air at 1 atm and room temperature, gives $n \sim 10^{25}$ m$^{-3}$ vs. $n_{\rm Q} \sim 10^{30}$ m$^{-3}$, will convince you that we can usefully stay out of that realm for a little longer.

### 11.10. *Thermodynamics of Classical Ideal Gas*

Finally, let us use (11.27), to extract the thermodynamics of ideal gas. The free energy is

$$\begin{aligned} F = -k_{\rm B}T\ln Z &= -k_{\rm B}T\left[N\ln\left(\frac{V}{\lambda_{\rm th}^3}\right) - \ln N!\right] \\ &\approx -k_{\rm B}T\left[\cancel{N\ln N} - N\ln(n\lambda_{\rm th}^3) - (\cancel{N\ln N} - N)\right] = -k_{\rm B}TN\left[1-\ln(n\lambda_{\rm th}^3)\right], \end{aligned} \tag{11.32}$$

where, upon application of Stirling's formula, the non-additive terms have happily cancelled.

The entropy is, therefore,

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_V = k_{\rm B}N\left[\frac{5}{2} - \ln(n\lambda_{\rm th}^3)\right]}\,, \tag{11.33}$$

[53] In other words, using (11.12), the number of states that are not exponentially unlikely is $\sim \int_0^{k_{\rm B}T} {\rm d}\varepsilon\, g(\varepsilon) \sim V/\lambda_{\rm th}^3$.

the formula known as the *Sackur–Tetrode Equation.* It is nice and additive, no paradoxes.

The mean energy of the gas is

$$U = F + TS = \frac{3}{2}\,k_{\rm B}TN, \tag{11.34}$$

the same as the familiar formula (2.23), and hence the heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}\,k_{\rm B}N, \tag{11.35}$$

the same as (2.24). Note that this result follows solely from how the single-particle partition function scales with $\beta$ (see §11.5).

*NB:* This formula is for *monatomic* gases. In Part IV, you will learn how to handle diatomic gases, where molecules can have additional energy levels due to rotational and vibrational degrees of freedom.

Finally, the equation of state is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_{\rm B}T\,\frac{N}{V} = nk_{\rm B}T, \tag{11.36}$$

the same as (2.19).

*NB:* The only property of the theory that matters for the equation of state is the fact that $Z \propto V^N$, so neither the (in)distinguishability of particles nor the precise form of the single-particle energy levels (11.4) affect the outcome—this will only change when particles start crowding each other out of parts of the volume, as happens for "real" gases (Part VII), or of parts of phase space, as happens for quantum ones (Part VI).

Thus, we have recovered from Statistical Mechanics the same thermodynamics for the ideal gas as was constructed empirically in Part I or kinetically in Part II. Note that (11.34) and (11.36) constitute the proof that *the kinetic temperature (2.20) and kinetic pressure (1.27) are the same as the statistical mechanical temperature ($= 1/k_{\rm B}\beta$) and statistical mechanical pressure (7.13).*

---

**Exercise 11.2. Adiabatic Law.** Using the Sackur–Tetrode equation, show that for a classical monatomic ideal gas undergoing an adiabatic process,

$$PV^{5/3} = \text{const}. \tag{11.37}$$

**Exercise 11.3. Flow of Entropy in an Adiabatic Gas.** Consider a Maxwellian gas described by the fluid equations derived in §6.4. Use the energy equation (6.37) and the continuity equation (6.17) to show that, if we neglect momentum and heat fluxes, the specific entropy, i.e., the entropy per particle $s = S/N$, satisfies the following equation[54]

$$\frac{\partial s}{\partial t} + \boldsymbol{u}\cdot\boldsymbol{\nabla}s = 0. \tag{11.38}$$

This equation describes what is known as an *adiabatic fluid* (in the context of this derivation, an ideal gas where each fluid element has no collisional collisional heat or momentum exchange with its neighbours and so each fluid element is an adiabatic system in a local equilibrium). Explain what this equation tells us physically about the dynamics of $s$ in such a fluid.

**Exercise 11.4. Relativistic Ideal Gas.** (a) Show that the equation of state of an ideal gas

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[54]The quantity $P/n^{5/3}$ [cf. (11.37)], which in fluid dynamics is also sometimes referred to as "specific entropy" (to which it is, in fact, related but not equal) satisfies the same equation. Convince yourself that this is true.

is still

$$PV = Nk_{\rm B}T \tag{11.39}$$

even when the gas is heated to such a high temperature that the particles are moving at relativistic speeds. Why is the equation of state unchanged?

(b) Although the equation of state does not change, show, by explicit calculation of the expression for the entropy, that in the ultrarelativistic limit (i.e., in the limit in which the rest energy of the particles is negligible compared to their kinetic energy), the formula for an adiabat is

$$PV^{4/3} = \text{const.} \tag{11.40}$$

(c) Show that the pressure of an ultrarelativistic monatomic ideal gas is

$$P = \frac{\varepsilon}{3}, \tag{11.41}$$

where $\varepsilon$ is the internal energy density. Why is this relationship different than for a nonrelativistic gas?

---

### 11.11. *Maxwell's Distribution*

Can we recover from Statistical Mechanics not just the thermodynamical quantities associated with the ideal gas, but also Maxwell's distribution itself? Certainly: the *particle distribution function* as we defined it in Part II is directly related to the *mean occupation number*. Indeed,

$f(\boldsymbol{v})\mathrm{d}^3\boldsymbol{v}$ = mean fraction of particles in microstates with velocities $[\boldsymbol{v}, \boldsymbol{v} + \mathrm{d}^3\boldsymbol{v}]$,

whereas

$\langle n_{\boldsymbol{k}}\rangle$ = mean number of particles in the microstate with wave number $\boldsymbol{k} = m\boldsymbol{v}/\hbar$.

Therefore,

$$f(\boldsymbol{v})\mathrm{d}^3\boldsymbol{v} = \frac{\langle n_{\boldsymbol{k}}\rangle}{N}\frac{V}{(2\pi)^3}\mathrm{d}^3\boldsymbol{k} = \frac{\langle n_{\boldsymbol{k}}\rangle}{n}\left(\frac{m}{2\pi\hbar}\right)^3\mathrm{d}^3\boldsymbol{v} \quad\Rightarrow\quad f(\boldsymbol{v}) = \left(\frac{m}{2\pi\hbar}\right)^3\frac{\langle n_{\boldsymbol{k}}\rangle}{n}. \tag{11.42}$$

We are not yet ready to calculate $\langle n_{\boldsymbol{k}}\rangle$ from Statistical Mechanics—we will do this in §16.3, but in the meanwhile, the anticipation of the Maxwellian $f(\boldsymbol{v})$ tells us what the result ought to be:

$$\langle n_{\boldsymbol{k}}\rangle = n\left(\frac{2\pi\hbar}{m}\right)^3\frac{e^{-mv^2/2k_{\rm B}T}}{(2\pi k_{\rm B}T/m)^{3/2}} = (n\lambda_{\rm th}^3)\,e^{-\beta\varepsilon_{\boldsymbol{k}}}. \tag{11.43}$$

We shall verify this formula in due course (see §16.4.3).

*NB:* It is a popular hand-waving shortcut to argue that Maxwell's distribution is the Gibbs distribution for one particle—a system in thermal contact (via collisions) with the rest of the particles, forming the heat bath and thus determining the particle's mean energy.

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## 12. P.S. Entropy, Ensembles and the Meaning of Probabilities

I have tried in the foregoing to take us as quickly as possible from the (perhaps somewhat murky) conceptual underpinnings of the Statistical Mechanics to a state of operational clarity as to how we would compute things. More things will be computed in Part IV.

Fortunately (or sadly), you do not need to *really* understand why maximising the expression $-\sum_\alpha p_\alpha \ln p_\alpha$ works or what it *really* means—you can simply embrace the straightforward Gibbs prescription:

1) compute $Z$ from knowledge of $\{\alpha\}$ and $\{E_\alpha\}$,
2) compute $F = -k_{\rm B}T\ln Z$,
3) compute $P, S, U$ from that (and $C_V$, usually),

4) move on to the next problem (in Statistical Mechanics or in life).

From this utilitarian viewpoint, my task of introducing the "Fundamentals of Statistical Mechanics" is complete. Nevertheless, in this section, I would like to discuss the notion of entropy and the meaning of $\{p_\alpha\}$ a little more and also to survey some alternative schemes for setting up Statistical Mechanics (they all eventually lead to the same practical prescriptions). This is for those of you who wish to make sense of the formalism and be convinced that we are on firm ground, intellectually—or are we?

## 12.1. *Boltzmann Entropy and the Ensembles*

### 12.1.1. *Boltzmann's Formula*

Ludwig Boltzmann's tombstone has a famous formula carved into it:

$$\boxed{S = k \log W}\,, \tag{12.1}$$

the "Boltzmann entropy," where $k$ is a constant (technically speaking, arbitrary $k > 0$, but traditionally $k_\mathrm{B}$, introduced, by the way, by Planck, not Boltzmann) and $W$ is "the number of complexions." What does this mean and how does it relate to what we have discussed so far?

A "complexion" is the same thing as I have so far referred to as a "state" ($\alpha$). So, Boltzmann's formula is for the entropy of a system in which all states/complexions are equiprobable (this is where the "equal *a priori* probabilities postulate," first mentioned in §8.1.1, comes in), so it is simply the same expression as we found for the case of all $p_\alpha = 1/\Omega$: then (12.1) has $W = \Omega$ and is the same as the familiar expression

$$S = k_\mathrm{B} \ln \Omega. \tag{12.2}$$

Boltzmann introduced his entropy following somewhat similar logic to that expressed by Shannon's theorem (which led to the Gibbs–Shannon entropy in §8.1.5): he wanted a function of $\Omega$ (the number of equiprobable states) that would be

1) larger for a larger number of states, viz., $S(\Omega') > S(\Omega)$ for $\Omega' > \Omega$,

2) additive for several systems when they are put together (an essential property, as we saw in §10), i.e., the number of states in a combined system being $\Omega_{12} = \Omega_1\Omega_2$, Boltzmann wanted

$$S(\Omega_1\Omega_2) = S(\Omega_1) + S(\Omega_2). \tag{12.3}$$

The proof that *the only such function is given by (12.2)* is the proof of the Lemma within the proof of Shannon's Theorem in §8.1.5.[55] Thus, Boltzmann's entropy simply appears to be a particular case of the Gibbs–Shannon entropy for isolated systems (systems with equiprobable states).

In fact, as we shall see in §§12.1.2 and 12.1.3, it is possible to turn the argument around and get the Gibbs entropy (and the Gibbs distribution) from the Boltzmann entropy.

### 12.1.2. *Microcanonical Ensemble*

This is an opportune moment to outline yet another way in which Statistical Mechanics and Thermodynamics can be constructed (as indeed they are, in the majority of

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[55] Thus, the uniqueness of the Gibbs–Shannon entropy as an adequate measure of uncertainty for a general probability distribution $\{p_\alpha\}$ is a corollary of the uniqueness of the Boltzmann entropy as an adequate measure of uncertainty for equiprobable outcomes. If you compare the proof of Shannon's theorem in §8.1.5 with the scheme for getting Gibbs entropy from Boltzmann entropy given at the end of §12.1.2, you will see the connection quite clearly.

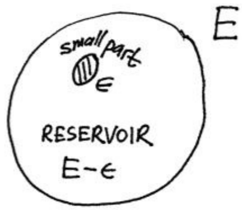


FIGURE 23. Small system inside a big reservoir.

textbooks). Effectively, this is an attempt to impart a veneer of "objective reality" to the foundations of the subject, which, in the way I have so far presented them, have perhaps been uncomfortably dependent on such seemingly subjective notions as the observer's information about the system.

Under this new scheme, we start by considering *a completely isolated system* and postulate (as we did in §8.1.1) that *all its microstates are equiprobable.*

Since the system is isolated, its energy is exactly conserved, so those microstates are, in fact, not *all* possible ones, but only those whose energies are equal to the exact energy of the system: $E_\alpha = E$. Their probabilities are then

$$\boxed{p_\alpha = \begin{cases} \dfrac{1}{\Omega(E)} & \text{if } E_\alpha = E, \\ 0 & \text{otherwise,} \end{cases}} \tag{12.4}$$

where $\Omega(E)$ is the total number of microstates with $E_\alpha = E$. This distribution is called *microcanonical* and the underlying ensemble of the realisations of the system, *the microcanonical ensemble.*[56] The entropy of this distribution is the Boltzmann entropy (§12.1.1):

$$\boxed{S = k_B \ln \Omega(E)}\,. \tag{12.5}$$

Now, to get the canonical (Gibbs) distribution from (12.4), pick a small part of the system (Fig. 23) and ask: what is the probability for it to have energy $\epsilon$ ($\ll E$)? Using (12.5) and denoting by

$\Omega_{\rm part}(\epsilon)$ the number of microstates of the small part of the system that have energy $\epsilon$,

$\Omega_{\rm res}(E-\epsilon)$ the number of microstates of the rest of the system (the reservoir, the heat bath; cf. §10.3) that have energy $E-\epsilon$,

[56]This can be generalised in a straightforward fashion to take into account the fact that an isolated system will also conserve its linear and angular momentum. In fact, it is possible to show that *in steady state* (and so, in equilibrium), the distribution can only be a function of globally conserved quantities. As it is usually possible to consider the system in a frame in which it is at rest, $E$ is what matters most in Statistical Mechanics (see, e.g., Landau & Lifshitz 1980, §4).

we can express the desired probability as follows:

$$
\begin{aligned}
p(\epsilon) = \frac{\Omega_{\rm part}(\epsilon)\Omega_{\rm res}(E-\epsilon)}{\Omega(E)} &= \frac{\Omega_{\rm part}(\epsilon)}{\Omega(E)}\,\exp\left\{\frac{S_{\rm res}(E-\epsilon)}{k_{\rm B}}\right\} \\
&\approx \frac{\Omega_{\rm part}(\epsilon)}{\Omega(E)}\,\exp\left\{\frac{1}{k_{\rm B}}\left[S_{\rm res}(E) - \epsilon\underbrace{\frac{\partial S_{\rm res}}{\partial E}}_{=1/T} + \dots\right]\right\} \\
&= \underbrace{\frac{e^{S_{\rm res}(E)/k_{\rm B}}}{\Omega(E)}}_{\substack{\text{norm.}\\ \text{constant}}}\,\Omega_{\rm part}(\epsilon)\, e^{-\epsilon/k_{\rm B}T},
\end{aligned}
\tag{12.6}
$$

where $T$ is, *by definition*, the temperature of the reservoir. The prefactor in front of this distribution is independent of $\epsilon$ and can be found by normalisation. Thus, we have obtained a variant of the Gibbs distribution (also known as the Boltzmann distribution):

$$
p(\epsilon) = \frac{\Omega_{\rm part}(\epsilon)\, e^{-\epsilon/k_{\rm B}T}}{Z}, \quad Z = \sum_\epsilon \Omega_{\rm part}(\epsilon)\, e^{-\epsilon/k_{\rm B}T},
\tag{12.7}
$$

where the normalisation constant has been cast in the familiar form of a partition function, $Z$. The reason that this formula, unlike (9.8), has the prefactor $\Omega(\epsilon)$ is that this is the probability for the system to have the energy $\epsilon$, not to occupy a particular single state $\alpha$. Many such states can have the same energy $\epsilon$—to be precise, $\Omega(\epsilon)$ of them will—all with the same probability, so we recover the more familiar formula as follows: for $\alpha$ such that the energy of the subsystem is $E_\alpha = \epsilon$,

$$
p_\alpha = \frac{p(\epsilon)}{\Omega_{\rm part}(\epsilon)} = \frac{e^{-\epsilon/k_{\rm B}T}}{Z} = \frac{e^{-\beta E_\alpha}}{Z}, \quad Z = \sum_\alpha e^{-\beta E_\alpha}.
\tag{12.8}
$$

We are done now, as we can again calculate everything from this: the mean energy via the usual formula

$$
U = -\frac{\partial \ln Z}{\partial \beta}
\tag{12.9}
$$

and entropy either by showing, as in §9.2, that

$$
dQ_{\rm rev} = dU + P dV = T d\left(\frac{U}{T} + k_{\rm B}\ln Z\right) = T dS_{\rm part},
\tag{12.10}
$$

so $T$ is the thermodynamic temperature and

$$
S_{\rm part} = \frac{U}{T} + k_{\rm B}\ln Z
\tag{12.11}
$$

the thermodynamic entropy of the small subsystem in contact with a reservoir of temperature $T$,

or by generalising Boltzmann's entropy in a way reminiscent of the requirement of additivity and independence of the state-counting scheme (criterion 5 in §8.1.5). Namely, if we demand

$$
\underbrace{S = k_{\rm B}\ln\Omega(E)}_{\substack{\text{total entropy of}\\ \text{isolated system}}} = \underbrace{S_{\rm part}}_{\substack{\text{entropy of}\\ \text{small part}}} + \underbrace{\langle S_{\rm res}(E-\epsilon)\rangle}_{\substack{\text{mean entropy}\\ \text{of reservoir}\\ (\text{over all }\epsilon)}},
\tag{12.12}
$$

then

$$S_{\rm part} = k_{\rm B}\ln\Omega(E) - \sum_\epsilon p(\epsilon)\underbrace{k_{\rm B}\ln\Omega_{\rm res}(E-\epsilon)}_{S_{\rm res}(E-\epsilon)}$$
$$= -k_{\rm B}\sum_\epsilon \underbrace{p(\epsilon)}_{=\,\Omega(\epsilon)p_\alpha}\ \ln\ \underbrace{\left[\frac{\Omega_{\rm res}(E-\epsilon)}{\Omega(E)}\right]}_{\substack{=\,p(\epsilon)/\Omega_{\rm part}(\epsilon)\\ =\,p_\alpha}} = -k_{\rm B}\sum_\alpha p_\alpha \ln p_\alpha, \tag{12.13}$$

and we have thus recovered the Gibbs entropy.

Let me reiterate an important feature of this approach: the microcanonical temperature was formally defined [see (12.6)] via the dependence of the (Boltzmann) entropy on the (exact) energy:

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E}}\,. \tag{12.14}$$

This quantity can then be given physical meaning in two (very similar) ways:

either we can repeat the argument of §10.2 replacing mean energies $U_1, U_2, U$ with exact energies $E_1, E_2, E$ and maximising the Boltzmann entropy of two conjoint systems to show that in equilibrium the quantity $T$ defined by (12.14) must equalise between them—and thus $T$ is a good definition of temperature.

or we note that $T$ defined via (12.14) is the width of the distribution $p(\epsilon)$ [see (12.7)] and hence enters (12.10)—thus, $1/T$ is manifestly the integrating factor of reversible heat, so $T$ is the thermodynamic temperature (same argument as in §9.2).

---

### 12.1.3. *Alternative (Original) Construction of the Canonical Ensemble*

[Literature: Schrödinger (1990)]

Finally, let me outline yet another scheme for constructing the Gibbs canonical ensemble.

Recall that in §8.1.3 we assigned $\mathcal{N}$ "quanta of probability" to $\Omega$ microstates in a "fair and balanced" fashion and found that the number of ways in which any particular set of probabilities $p_\alpha = \mathcal{N}_\alpha/\mathcal{N}$ could be obtained was [see (8.4)]

$$W = \frac{\mathcal{N}!}{\mathcal{N}_1!\cdots\mathcal{N}_\Omega!}; \tag{12.15}$$

the entropy then was simply [see (8.7)]

$$S = \frac{k_{\rm B}\ln W}{\mathcal{N}} = -k_{\rm B}\sum_\alpha p_\alpha\ln p_\alpha \tag{12.16}$$

(with all $\mathcal{N}, \mathcal{N}_\alpha \to \infty$ while keeping $\mathcal{N}_\alpha/\mathcal{N} = p_\alpha = \text{const}$). This was justified as a counting scheme: larger $W$ gave the more probable assignment of $p_\alpha$'s and then it was convenient to take a log to make $S$ additive. At that stage, I presented this scheme simply as a "reasonable" procedure. In §8.1.5, I removed the need for us to believe in its "reasonableness" by showing that the Gibbs-Shannon expression for $S$ was in a certain sense the uniquely suitable choice.

This is *not*, in fact, how the Gibbs construction has traditionally been thought about (e.g., by Gibbs 1902—or by Schrödinger 1990, who has a very cogent explanation of the more traditional approach in his lectures). Rather,

- one makes $\mathcal{N}$ mental copies of the system that one is interested in and joins them together into one *isolated* über-system (an "ensemble"). The states ("complexions") of this über-system are characterised by

$\mathcal{N}_1$ copies of the original system being in the state $\alpha = 1$,
$\mathcal{N}_2$ copies of the original system being in the state $\alpha = 2$,
...
$\mathcal{N}_\Omega$ copies of the original system being in the state $\alpha = \Omega$,

and so the number of all possible such über-states is $W$, given by (12.15).

• Since the über-system is isolated, all these states are equiprobable and the entropy of the über-system is the Boltzmann entropy,

$$S_{\mathcal{N}} = k_{\mathrm{B}} \ln W, \tag{12.17}$$

which, if maximised, will give the most probable über-state—this is the equilibrium state of the über-system. Maximising entropy *per system*,

$$S = \frac{S_{\mathcal{N}}}{\mathcal{N}}, \tag{12.18}$$

which is the same as Gibbs entropy (12.16), is equivalent to maximising $S_{\mathcal{N}}$.

• If $\{N_1, \dots, N_\Omega\}$ is the most probable über-state, then

$$p_\alpha = \frac{\mathcal{N}_\alpha}{\mathcal{N}} \tag{12.19}$$

are the desired probabilities of the microstates in which one might find a copy of the original system if one picks it randomly from the über-system (the ensemble).

• To complete this construction, one proves that the fluctuations around the most probable über-state vanish as $\mathcal{N} \to \infty$, which is always a good limit because $\mathcal{N}$ is in our head and so can be chosen arbitrarily large (for details, see Schrödinger 1990, Chapter V, VI).

Recall that to get the canonical (Gibbs) distribution (§9.1), we maximised Gibbs entropy [see (12.18), or (12.16)] subject to fixed *mean energy*

$$\sum_\alpha p_\alpha E_\alpha = U. \tag{12.20}$$

In view of (12.19), this is the same as

$$\sum_\alpha \mathcal{N}_\alpha E_\alpha = \mathcal{N} U = \mathcal{E}, \tag{12.21}$$

i.e., the (isolated) über-system has the *exact* total energy $\mathcal{E} = \mathcal{N}U$. Thus, *seeking the equilibrium of a system at fixed mean energy $U$ (or, equivalently/consequently, temperature) is the same as seeking the most likely way in which exact energy $\mathcal{N}U$ would distribute itself between very many, $\mathcal{N} \gg 1$, copies of the system, if they were all in thermal contact with each other and isolated from the rest of the world.*

Thus, the canonical ensemble of Gibbs, if interpreted in terms of one "über-system" containing $\mathcal{N}$ copies of the original system with exact total energy $\mathcal{N}U$ is basically a case of microcanonical distribution being applied to this (imaginary) assemblage.

Clearly, a system with mean energy $U$ inside our über-system is a case of *a system in contact with a heat bath* (see §10.3)—in the above construction, the bath is a strange one, as it is made of $\mathcal{N} - 1$ copies of the system itself, but that does not matter because the nature of the heat bath does not matter—what does matter is only the value of the temperature (or, equivalently, mean energy) that it sets for the system.

## 12.2. *Gibbs vs. Boltzmann and the Meaning of Probabilities*

Let us summarise the three main schemes for the construction of Statistical Mechanics and Thermodynamics that we have learned.

| "BOLTZMANN" (and most textbooks) see §12.1.2 | "GIBBS" (and Schrödinger 1990) see §12.1.3 | "SHANNON" (and Jaynes 2003) see §§9.1 and 8.1.5 |
|---|---|---|
| • Consider a completely isolated system with fixed exact energy $E$. • Assume equal probabilities for all its states. | • Imagine an ensemble of $\mathcal{N}$ identical copies of the system in thermal contact. • Distribute energy $\mathcal{N}U$ between them. | • Admit nearly total ignorance about the system. • Seek statistical inference about likelihoods of states subject to a few scraps of knowledge (the value of $U$) and no other bias. |
| ⇕ | ⇕ | ⇕ |
| Microcanonical ensemble | Canonical ensemble | |
| • Consider a small subsystem. | • Maximise Gibbs entropy subject to fixed mean energy $U$. | Maximise Shannon entropy subject to constraints imposed by that knowledge. |
| ⇓ | ⇓ | ⇓ |

Get Gibbs distribution (9.8) as the outcome of any of these three schemes.

⇓

Calculate everything ($U$, $S$, $F$, etc.).

⇓

Get testable results and test them experimentally.

The "Gibbs" and "Shannon" schemes really are versions of one another: whereas the language is different, both the mathematics (cf. §§8.1.3 and 12.1.3) and the philosophy (probabilities as *likelihoods* of finding the system of interest in any given microstate) are the same (one might even argue that the "Shannon" construction is what Gibbs really had in mind). So I will refer to this entire school of thought as "Gibbsian" (perhaps the "Gibbsian heresy").

The Boltzmann scheme (the "Boltzmannite orthodoxy") is philosophically different: we are invited to think of every step in the construction as describing some form of objective reality, whereas under the Gibbsian approach, we are effectively just trying to come up with the best possible guess, given limited information.

The reality of the Boltzmannite construction is, however, somewhat illusory:

1) *An isolated system with a fixed energy is a fiction:*
—it is impossible to set up practically;
—if set up, it is inaccessible to measurement (because it is isolated!).
So it is in fact just as imaginary as, say, the Gibbsian ensemble of $\mathcal{N}$ identical systems.

2) *What is the basis for assuming equal probabilities?*
The usual view within this school of thought is as follows. As the isolated system in question evolves in time, it samples (repeatedly) its entire phase space—i.e., it visits all possible microstates consistent with its conservation laws ($E = \text{const}$). Thus, *the probability for it to be in any given microstate or set of microstates is simply the fraction of time that it spends in those states.* In other words, *time averages* of any quantities of interest are equal to the *statistical averages*, i.e., to the averages over all microstates:

$$\lim_{t\to\infty}\frac{1}{t}\int_0^t dt'(\text{quantity})(t') = \sum_\alpha p_\alpha(\text{quantity})_\alpha. \tag{12.22}$$

This last statement is known as the *ergodic hypothesis.* To be precise, the assumption is that

$$\begin{array}{c}\text{time spent in any subset of}\\ \text{microstates}\\ \text{(subvolume of phase space)}\end{array} = \frac{\text{number of microstates in this subset}}{\text{total number of microstates}}. \tag{12.23}$$

So the idea is that we do all our practical calculations via statistical averages (with $p_\alpha = 1/\Omega$

etc.), but the physical justification for that is that the system is time-averaging itself (we cannot directly calculate time averages because we cannot calculate precise dynamics).[57]

The objection to this view that I find the most compelling is simply that the size of the phase space (the number of microstates) of any macroscopic system is so enormous that it is in fact quite impossible for the system to visit all of it over a reasonable time (see Jaynes 2003).

The key divide here is rooted in the old argument about the meaning of probabilities:

—probabilities as frequencies, or "objective" probabilities, measuring how often something actually happens

vs.

—probabilities as (*a priori*) likelihoods, or "subjective" probabilities, measuring our (lack of) knowledge about what happens (this view has quite a respectable intellectual pedigree: Laplace, Bayes, Keynes, Jeffreys, Jaynes... and Binney!).

> *NB:* In choosing to go with the latter view and putting up all these objections to the former, I am not suggesting that one is "right" and the other "wrong." Remember that the falsifiable (and examinable) content of the theory is the same either way, so the issue is which of the logical constructions leading to it makes more sense to me or to you—and I urge you to explore the literature on your own and decide for yourselves whether you are a Gibbsian or a Boltzmannite (either way, you are in good company)—or, indeed, whether you wish to invent a third way![58]

## 12.3. *Whose Uncertainty?*

[Literature: Jaynes (2003), §11.8]

To pre-empt some of the inevitable confusion about the "subjective" nature of maximising uncertainty (*whose* uncertainty?!), let me deal with the common objection that, surely, if two observers (call them A and B) have different amounts of information about the same system and so arrive at two different entropy-maximising sets of $p_\alpha$'s, it would be disastrous if those different sets gave different testable predictions about the system! (Heat capacity of a room filled with air cannot depend on who is looking!)

There are three possible scenarios.

• If Mrs B has more constraints (i.e., more knowledge) than Mr A, but her additional constraints are, in fact, *derivable* from Mr A's, then both Mr A and Mrs B will get the same probability distribution $\{p_\alpha\}$ because Mrs B's additional Lagrange multipliers will turn out to be arbitrary and so can be set to 0 (this is easy to see if you work through an example: e.g., Exercise 9.1e).

• If Mrs B's additional constraints are *incompatible* with Mr A's, the method of Lagrange multipliers will produce a set of equations for $\lambda$'s that has no real solutions (and so no real $p_\alpha$'s)—telling us that the system of constraints is logically contradictory and so no theory exists (this basically means that one of them got their constraints wrong).

[57] A further mathematical nuance is as follows. Formally speaking, the system over which we are calculating the averages, e.g., in the case of the ideal gas, often consists of a number of non-interacting particles—since they are non-interacting, each of them conserves its energy and the system is most definitely *not* ergodic: its phase space is foliated into many subspaces defined by the constancy of the energy of each particle and the system cannot escape from any of these subspaces. To get around this problem, one must assume that the particles in fact do interact (indeed, they collide!), but rarely, so their interaction energy is small. If we calculate the time average in the left-hand side of (12.22) for this weakly interacting system, then the resulting average taken in the limit of vanishing interaction will be equal to the statistical average on the right-hand side of (12.22) calculated for the system with no interaction (see, e.g., Berezin 2007, §2; he also makes the point that as the interaction energy tends to zero, the rate of convergence of the time average to a finite value as $t \to \infty$ may become very slow, in which case the physical value of the ergodic hypothesis becomes rather limited—this reinforces Jaynes's objection articulated in the next paragraph).

[58] This is a bit like the thorny matter of the interpretations of Quantum Mechanics: everyone agrees on the results, but not on why the theory works.

• Finally, if Mrs B's additional constraints are neither incompatible with nor derivable from Mr A's, that means that she has discovered new physics: Mrs B's additional constraints will bring in new Lagrange multipliers, which will turn out to have some interesting physical interpretation—usually as some macroscopic thermodynamical quantities (we will see an example of this when we discover chemical potential in §14).

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### 12.4. *Second Law*

[Literature: Jaynes (1965)]

So far in this part of the course, we have not involved time in our considerations: we have always been interested in some eventual equilibrium and the way to calculate it was to maximise $S_G$ subject to constraints representing some measurable properties of this equilibrium. This maximisation of $S_G$ is *not* the same thing as the 2-nd Law of Thermodynamics, which states, effectively, that *the thermodynamic entropy $S$ of the world (or a closed, isolated system) must either increase or stay constant in any process—and so in time.*

This statement is famously replete with hard metaphysical questions (even though it is quite straightforward when it comes to calculating entropy changes in mundane situations)—so it is perhaps useful to see how it emerges within the conceptual framework that I am advocating here. The following proof is what I believe to be an acceptable vulgarisation of an argument due to Jaynes (1965).

Time $t$:

Consider a closed system (the world) in equilibrium, subject to some set of its properties having just been measured and no other information available. Then our best guess as to its state at this time $t$ is obtained by maximising $S_G$ subject to those properties that are known at time $t$. This gives a set of probabilities $\{p_\alpha\}$ that describe this equilibrium. In this equilibrium, the maximum value of $S_G$ that we have obtained is equal to the thermodynamical entropy (see proof in §9.2):

$$S(t) = k_B S_{G,\max}(t). \tag{12.24}$$

Time $t' > t$:

Now consider the evolution of this system from time $t$ to a later time $t'$, starting from the set of states $\{\alpha\}$ and their probabilities $\{p_\alpha\}$ that we inferred at time $t$ and using Hamilton's equations (if the system is classical) or the time-dependent Schrödinger's equation (if it is quantum, as it always really is; see §13.4). During this evolution, *the Gibbs entropy stays constant:*

$$S_G(t') = -\sum_\alpha p_\alpha \ln p_\alpha = S_G(t). \tag{12.25}$$

Indeed, the Schrödinger equation evolves the states $\{\alpha\}$, but if the system was in some state $\alpha(t)$ at time $t$ with probability $p_\alpha$, it will be in the descendant $\alpha(t')$ of that state at $t'$ with exactly the same probability; this is like changing labels in the expression for $S_G$ while $p_\alpha$'s stay the same—and so does $S_G$. Thus,

$$S_G(t') = S_G(t) = S_{G,\max}(t) = \frac{1}{k_B} S(t). \tag{12.26}$$

Now forget all previous information, make a new set of measurements at time $t'$, work out a new set of probabilities $\{p_\alpha\}$ at $t'$ subject only to these new constraints, by maximising Gibbs entropy, and from it infer the new thermodynamical (equilibrium) entropy:

$$S(t') = \underbrace{k_B S_{G,\max}(t')}_{\substack{\text{the new } S_G,\\ \text{maximised at}\\ \text{time } t'}} \geqslant \underbrace{k_B S_G(t')}_{\substack{\text{the "true"}\\ S_G,\text{ evolved}\\ \text{from time } t}} = k_B S_G(t) = S(t). \tag{12.27}$$

Thus,

$$\boxed{S(t') \geqslant S(t)} \text{ at } t' > t, \text{ q.e.d., Second Law.} \tag{12.28}$$

*The meaning of this is that the increase of $S$ reflects our insistence to forget most of the detailed knowledge that we possess as a result of evolving in time any earlier state (even if based on an earlier guess) and to re-apply at every later time the rules of statistical inference based on the very little knowledge that we can obtain in our measurements at those later times.*

If you are sufficiently steeped in quantum ways of thinking by now, you will pounce and ask: who is doing all these measurements?

If it is an external observer or apparatus, then the system is not really closed and, in particular, the measurement at the later time $t'$ will potentially destroy the identification of all those microstates with their progenitors at time $t$, so the equality (12.25) no longer holds.[59]

A further objection is: what if your measurements at $t'$ are much better than at the technologically backward time $t$? You might imagine an extreme case in which you determine the state of the system at $t'$ precisely and so $S_G(t') = 0$!

• Clearly, the observer is, in fact, not external, but lives inside the system.

• As he/she/they perform the measurement, not just the entropy of the object of measurement (a subsystem) but also of the observer and their apparatus changes. The argument above implies that a very precise measurement leading to a decrease in the entropy of the measured subsystem must massively increase the entropy of the observer and his kit, to compensate, and thus ensure that the total entropy increases as per (12.28).[60]

I will return to these arguments in a slightly more quantitative (or, at any rate, more quantum) manner in §§13.4–13.5.

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## 13. P.P.S. Density Matrix and Entropy in Quantum Mechanics

[Literature: Binney & Skinner (2013), §6.3, 6.5]

So far the only way in which the quantum-mechanical nature of the world has figured in our discussion is via the sums of states being discrete and also in the interpretation of the indistinguishability of particles. Now I want to show you how one introduces the uncertainty about the quantum state of the system into the general quantum mechanical formalism.

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[59]In a classical world, this would not be a problem because you can make measurements without altering the system, but in Quantum Mechanics, you cannot.

[60]This sort of argument was the basis of the exorcism of Maxwell's Demon by Szilard (1929).

### 13.1. *Statistical and Quantum Uncertainty*

Suppose we are uncertain about the quantum state of our system but think that it is in one of a *complete set of orthogonal quantum states* $\{|\alpha\rangle\}$ ($\alpha = 1, \dots, \Omega$) and our uncertainty about which one it is is expressed by *a priori* probabilities $\{p_\alpha\}$, as usual (assigned via the entropy-maximising procedure whose quantum further particulars I am about to explain).[61] For any *observable* $\hat{O}$ (which is an operator, e.g., the Hamiltonian $\hat{H}$), its expectation value is

$$\bar{O} = \sum_\alpha p_\alpha \langle\alpha|\hat{O}|\alpha\rangle, \tag{13.1}$$

$p_\alpha$ is the *a priori* probability that the system is in the state $|\alpha\rangle$ and $\langle\alpha|\hat{O}|\alpha\rangle$ is the expectation value of $\hat{O}$ *if* the system is in the state $|\alpha\rangle$ (e.g., $E_\alpha$ if $\hat{O} = \hat{H}$). The states $\{|\alpha\rangle\}$ are *not* necessarily eigenstates of $\hat{O}$. Since, written in terms of its eigenstates and eigenvalues, this operator is

$$\hat{O} = \sum_\mu O_\mu |O_\mu\rangle\langle O_\mu|, \tag{13.2}$$

its expectation value (13.1) can be written as

$$\bar{O} = \sum_{\alpha\mu} p_\alpha O_\mu \langle\alpha|O_\mu\rangle\langle O_\mu|\alpha\rangle = \sum_\mu O_\mu \underbrace{\sum_\alpha p_\alpha |\langle O_\mu|\alpha\rangle|^2}_{\substack{\text{total}\\ \text{probability to}\\ \text{measure } O_\mu}}. \tag{13.3}$$

This formula underscores the fact that the expected outcome of a measurement is subject to two types of uncertainty:

—our uncertainty as to what state the system is in (quantified by the probability $p_\alpha$ to be in the state $|\alpha\rangle$),

—quantum (intrinsic) uncertainty as to the outcome of a measurement, given a definite quantum state (this uncertainty is quantified by $|\langle O_\mu|\alpha\rangle|^2$, the probability to measure $O_\mu$ if the system is in the state $|\alpha\rangle$).

### 13.2. *Density Matrix*

This construction motivates us to introduce the *density operator*

$$\boxed{\hat{\rho} = \sum_\alpha p_\alpha |\alpha\rangle\langle\alpha|}\,. \tag{13.4}$$

This looks analogous to (13.2), except note that $\hat{\rho}$ is *not* an observable because $p_\alpha$'s are subjective. In the context of this definition, one refers to the system being in a *pure state* if for some $\alpha$, $p_\alpha = 1$ and so $\hat{\rho} = |\alpha\rangle\langle\alpha|$, or an *impure state* if all $p_\alpha < 1$.

The density operator is useful because, knowing $\hat{\rho}$, we can express expectation values of observables as

$$\boxed{\bar{O} = \mathrm{Tr}\big(\hat{\rho}\hat{O}\big)}. \tag{13.5}$$

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[61] It is an interesting question whether it is important that the system *really* is in one of the states $\{|\alpha\rangle\}$. Binney & Skinner (2013) appear to think it is important to conjecture this, but I am unconvinced. Indeed, in the same way that probabilities $p_\alpha$ are not the true quantum probabilities but rather a set of probabilities that would produce correct predictions for measurement outcomes (expectation values $\bar{O}$), it seems natural to allow $\{|\alpha\rangle\}$ to be any complete set, with $p_\alpha$ then chosen so that measurement outcomes are correctly predicted. This does raise the possibility that if our measurement were so precise as to pin down the true state of the system unambiguously, it might not be possible to accommodate such information with any set of $p_\alpha$'s. However, such a situation would correspond to complete certainty anyway, obviating statistical approach.

Indeed, the above expression reduces to (13.1):

$$\mathrm{Tr}\big(\hat{\rho}\,\hat{O}\big) = \sum_{\alpha'}\langle\alpha'|\hat{\rho}\hat{O}|\alpha'\rangle = \sum_{\alpha'\alpha} p_\alpha \underbrace{\langle\alpha'|\alpha\rangle}_{\delta_{\alpha'\alpha}} \langle\alpha|\hat{O}|\alpha'\rangle = \sum_\alpha p_\alpha \langle\alpha|\hat{O}|\alpha\rangle = \bar{O}, \quad \text{q.e.d.} \tag{13.6}$$

It is useful to look at the density operator in the $\{|O_\mu\rangle\}$ representation: since

$$|\alpha\rangle = \sum_\mu \langle O_\mu|\alpha\rangle|O_\mu\rangle, \tag{13.7}$$

we have

$$\hat{\rho} = \sum_\alpha p_\alpha \sum_{\mu\nu}\langle O_\mu|\alpha\rangle\langle\alpha|O_\nu\rangle|O_\mu\rangle\langle O_\nu| \equiv \sum_{\mu\nu} p_{\mu\nu}|O_\mu\rangle\langle O_\nu|, \tag{13.8}$$

where we have introduced the *density matrix:*

$$\boxed{p_{\mu\nu} = \sum_\alpha p_\alpha \langle O_\mu|\alpha\rangle\langle\alpha|O_\nu\rangle}\,. \tag{13.9}$$

Thus, whereas $\hat{\rho}$ is diagonal in the "information basis" $\{|\alpha\rangle\}$, it is, in general, *not* diagonal in any given basis associated with the eigenstates of an observable, $\{|O_\mu\rangle\}$—in other words, the states to which we assign *a priori* probabilities are not necessarily the eigenstates of the observable that we then wish to calculate.

Let us express the expectation value of $\hat{O}$ in terms of the density matrix: using (13.8),

$$\bar{O} = \mathrm{Tr}\big(\hat{\rho}\,\hat{O}\big) = \sum_{\mu'}\langle O_{\mu'}|\hat{\rho}\hat{O}|O_{\mu'}\rangle = \sum_{\mu'\mu\nu} O_{\mu'} p_{\mu\nu} \underbrace{\langle O_{\mu'}|O_\mu\rangle}_{\delta_{\mu'\mu}} \underbrace{\langle O_\nu|O_{\mu'}\rangle}_{\delta_{\nu\mu'}} = \sum_\mu O_\mu p_{\mu\mu}, \tag{13.10}$$

the same expression as (13.3), seeing that

$$p_{\mu\mu} = \sum_\alpha p_\alpha |\langle O_\mu|\alpha\rangle|^2. \tag{13.11}$$

Thus, the diagonal elements of the density matrix in the $\hat{O}$ representation are the combined quantum and *a priori* (statistical) probabilities of the observable giving eigenvalues $O_\mu$ as measurement outcomes.

The off-diagonal elements have no classical interpretation. They measure quantum correlations and come into play when, e.g., we want the expectation value of an observable other than the one in whose representation we chose to write $\hat{\rho}$: for an observable $\hat{P}$, the expectation value is

$$\bar{P} = \mathrm{Tr}\big(\hat{\rho}\,\hat{P}\big) = \sum_{\mu'}\langle O_{\mu'}|\underbrace{\sum_{\mu\nu} p_{\mu\nu}|O_\mu\rangle\langle O_\nu|}_{\hat{\rho}}\,\hat{P}|O_{\mu'}\rangle = \sum_{\mu\nu} p_{\mu\nu}\langle O_\nu|\hat{P}|O_\mu\rangle. \tag{13.12}$$

### 13.3. *Quantum Entropy and Canonical Ensemble*

The generalisation of the Gibbs–Shannon entropy in this formalism is the *von Neumann entropy*:

$$\boxed{S_{\mathrm{vN}} = -\mathrm{Tr}\big(\hat{\rho}\,\ln\hat{\rho}\big)}\,, \tag{13.13}$$

which is, in fact, the same as $S_{\mathrm{G}}$:

$$\begin{aligned} S_{\mathrm{vN}} &= -\sum_\alpha \langle\alpha|\underbrace{\left(\sum_\mu p_\mu|\mu\rangle\langle\mu|\right)}_{\hat{\rho}}\underbrace{\left(\sum_\nu \ln p_\nu|\nu\rangle\langle\nu|\right)}_{\substack{\ln\hat{\rho},\\ \text{by definition}}}|\alpha\rangle \\ &= -\sum_{\alpha\mu\nu} p_\mu \ln p_\nu \underbrace{\langle\alpha|\mu\rangle}_{\delta_{\alpha\mu}}\underbrace{\langle\mu|\nu\rangle}_{\delta_{\mu\nu}}\underbrace{\langle\nu|\alpha\rangle}_{\delta_{\nu\alpha}} = -\sum_\alpha p_\alpha \ln p_\alpha. \end{aligned} \tag{13.14}$$

As always, we find $p_\alpha$'s by maximising $S_{\rm vN}$ subject to constraints imposed by the information that we possess, often in the form of expectation values like $\bar{O}$.

The canonical distribution (9.8) has the following density matrix, *in energy representation*:

$$\hat{\rho} = \sum_\alpha \frac{e^{-\beta E_\alpha}}{Z} |\alpha\rangle\langle\alpha| = \frac{e^{-\beta\hat{H}}}{Z}, \tag{13.15}$$

where $\{|\alpha\rangle\}$ are understood to be eigenstates of $\hat{H}$ and the partition function is

$$Z = \sum_\alpha e^{-\beta E_\alpha} = \mathrm{Tr}\, e^{-\beta\hat{H}} \tag{13.16}$$

## 13.4. *Time Evolution and the Second Law*

If we know $\hat{\rho}$ at some time, we can easily find it at any later time:

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = \sum_\alpha p_\alpha \left( \frac{\partial|\alpha\rangle}{\partial t}\langle\alpha| + |\alpha\rangle\frac{\partial\langle\alpha|}{\partial t} \right) = \frac{1}{i\hbar}\sum_\alpha p_\alpha \left(\hat{H}|\alpha\rangle\langle\alpha| - |\alpha\rangle\langle\alpha|\hat{H}\right) = \frac{\hat{H}\hat{\rho} - \hat{\rho}\hat{H}}{i\hbar} \tag{13.17}$$

is the *time-dependent Schrödinger equation*. In a more standard form:

$$\boxed{i\hbar\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = [\hat{H}, \hat{\rho}]}\,. \tag{13.18}$$

Note that the probabilities $p_\alpha$ do not change with time: if the system was in a state $|\alpha(0)\rangle$ initially, it will be in its descendant state $|\alpha(t)\rangle$ at any later time $t$.

So, we may envision a situation in which *we are uncertain about a system's initial conditions*, work out $\hat{\rho}(t=0)$ via the maximum-entropy principle, constrained by some measurements, and then evolve $\hat{\rho}(t)$ forever *if* we know the Hamiltonian precisely. Since $p_\alpha$'s do not change, *the Gibbs–Shannon–von Neumann entropy of the system stays the same during this time evolution*—the only uncertainty was in the initial conditions.

What if we do not know the Hamiltonian (or choose to forget)? This was discussed in §12.4: then, at a later time, we may make another measurement and construct the new density matrix $\hat{\rho}_{\rm new}(t)$ via another application of the maximum-entropy principle. Both $\hat{\rho}_{\rm new}(t)$ and $\hat{\rho}_{\rm old}(t)$—which is our $\hat{\rho}(0)$ evolved via (13.18) with the (unknown to us) precise $\hat{H}$—are consistent with the new measurement. But $\hat{\rho}_{\rm new}(t)$ corresponds to the maximum possible value of the entropy consistent with this measurement, while $\hat{\rho}_{\rm old}(t)$ has the same entropy as $\hat{\rho}(0)$ did at $t=0$. Therefore,

$$S_{\rm new}(t) > S_{\rm old}(0). \tag{13.19}$$

This is the Second Law and the argument above is the same as the argument already given in §12.4.

## 13.5. *How Information Is Lost*

When we discuss predictions or outcomes of physical measurements, we can think of the world as consisting of two parts:

—the system to be measured,

—the rest of the world: the environment, including the measurement apparatus (sometimes only it if the experiment is "isolated").

The observables that we have and so the information that we will use for statistical inference will pertain to the system, while the environment will remain mysterious.

For example, imagine that we measured the energy of the system at some initial time. For lack of better knowledge, it is natural to make a statistical inference about the microstates of the world in the following form:

$$|\alpha\alpha', 0\rangle = |E_\alpha^{(\rm sys)}(0)\rangle|E_{\alpha'}^{(\rm env)}(0)\rangle, \tag{13.20}$$

where 0 stands for $t=0$, $|E_\alpha^{(\rm sys)}(0)\rangle$ are the states of the system in the energy representation and $|E^{(\mathrm{env})}_{\alpha'}(0)\rangle$ are the states of the environment (unknown). Then

$$\hat{\rho}(0) = \sum_{\alpha\alpha'} p_{\alpha\alpha'}|\alpha\alpha',0\rangle\langle\alpha\alpha',0|, \tag{13.21}$$

where $p_{\alpha\alpha'}$ are the probabilities of $|E^{(\mathrm{sys})}_{\alpha}(0)\rangle$, indifferent to $|E^{(\mathrm{env})}_{\alpha'}(0)\rangle$.

Now evolve this density matrix according to the time-dependent Schrödinger equation (13.18): $p_{\alpha\alpha'}$'s will stay the same, while the states will evolve:

$$|\alpha\alpha',0\rangle \to |\alpha\alpha',t\rangle \neq |E^{(\mathrm{sys})}_{\alpha}(t)\rangle|E^{(\mathrm{env})}_{\alpha'}(t)\rangle. \tag{13.22}$$

The descendants of the initial states (13.20) will *not* in general be superpositions of the energy states of the system and the environment. This is because the system and the environment get *entangled*. Formally speaking,

$|E^{(\mathrm{sys})}_{\alpha}\rangle$ are eigenstates of $\hat{H}^{(\mathrm{sys})}$, the Hamiltonian of the system,
$|E^{(\mathrm{env})}_{\alpha'}\rangle$ are eigenstates of $\hat{H}^{(\mathrm{env})}$, the Hamiltonian of the environment,

but

$|E^{(\mathrm{sys})}_{\alpha}\rangle|E^{(\mathrm{env})}_{\alpha'}\rangle$ are *not* eigenstates of the world's Hamiltonian:

$$\hat{H} = \hat{H}^{(\mathrm{sys})} + \hat{H}^{(\mathrm{env})} + \hat{H}^{(\mathrm{int})} \tag{13.23}$$

because of the interaction Hamiltonian $\hat{H}^{(\mathrm{int})} \neq 0$.

If, at time $t$, we measure the energy of the system again, we will have to make statistical inference about superposed eigenstates:

$$|\alpha\alpha',\mathrm{new}\rangle = |E^{(\mathrm{sys})}_{\alpha}(t)\rangle|E^{(\mathrm{env})}_{\alpha'}(t)\rangle \neq |\alpha\alpha',t\rangle. \tag{13.24}$$

In this new representation, our old density matrix is *no longer diagonal*:

$$\begin{aligned}\hat{\rho}^{(\mathrm{old})}(t) &= \sum_{\alpha\alpha'} p^{(\mathrm{old})}_{\alpha\alpha'}|\alpha\alpha',t\rangle\langle\alpha\alpha',t| \\ &= \sum_{\alpha\alpha'} p^{(\mathrm{old})}_{\alpha\alpha'}\sum_{\mu\mu'}\sum_{\nu\nu'}|\mu\mu',\mathrm{new}\rangle\langle\mu\mu',\mathrm{new}|\alpha\alpha,t\rangle\langle\alpha\alpha',t|\nu\nu',\mathrm{new}\rangle\langle\nu\nu',\mathrm{new}| \\ &= \sum_{\mu\mu'}\sum_{\nu\nu'} p^{(\mathrm{old})}_{\mu\mu'\nu\nu'}(t)|\mu\mu',\mathrm{new}\rangle\langle\nu\nu',\mathrm{new}|,\end{aligned} \tag{13.25}$$

where the old density matrix in the new representation is [cf. (13.9)]:

$$p^{(\mathrm{old})}_{\mu\mu'\nu\nu'}(t) = \sum_{\alpha\alpha'} p^{(\mathrm{old})}_{\alpha\alpha'}\langle\mu\mu',\mathrm{new}|\alpha\alpha,t\rangle\langle\alpha\alpha',t|\nu\nu',\mathrm{new}\rangle. \tag{13.26}$$

However, the measured energy of the system at time $t$ only depends on the diagonal elements $p^{(\mathrm{old})}_{\alpha\alpha'\alpha\alpha'}(t)$ of this matrix:

$$\begin{aligned}U &= \mathrm{Tr}\left[\hat{\rho}^{(\mathrm{old})}(t)\hat{H}^{(\mathrm{sys})}(t)\right] \\ &= \sum_{\alpha\alpha'}\sum_{\mu\mu'}\sum_{\nu\nu'} p^{(\mathrm{old})}_{\mu\mu'\nu\nu'}(t)E^{(\mathrm{sys})}_{\nu}(t)\langle\alpha\alpha',\mathrm{new}|\mu\mu',\mathrm{new}\rangle\langle\nu\nu',\mathrm{new}|\alpha\alpha',\mathrm{new}\rangle \\ &= \sum_{\alpha\alpha'} p^{(\mathrm{old})}_{\alpha\alpha'\alpha\alpha'}(t)E^{(\mathrm{sys})}_{\alpha}(t).\end{aligned} \tag{13.27}$$

*All information about correlations between the system and the environment is lost in this measurement.*

When we maximise entropy and thus make a new statistical inference about the system, the new entropy will be higher than the old for two reasons:

(1) all off-diagonal elements from the old density matrix are lost,

(2) the diagonal elements $p^{(\mathrm{old})}_{\alpha\alpha'\alpha\alpha'}(t)$ are in general *not* the ones that maximise entropy (see

the argument in §12.4):

$$p^{(\mathrm{new})}_{\alpha\alpha'} \neq p^{(\mathrm{old})}_{\alpha\alpha'\alpha\alpha'}(t). \tag{13.28}$$

Thus, the new density matrix

$$\hat{\rho}^{(\mathrm{new})} = \sum_{\alpha\alpha'} p^{(\mathrm{new})}_{\alpha\alpha'} |\alpha\alpha', \mathrm{new}\rangle\langle\alpha\alpha', \mathrm{new}|, \tag{13.29}$$

being the maximiser of entropy at time $t$, will have

$$S^{(\mathrm{new})}_{\mathrm{vN}} = -\mathrm{Tr}\left[\hat{\rho}^{(\mathrm{new})} \ln \hat{\rho}^{(\mathrm{new})}\right] \geqslant S^{(\mathrm{old})}_{\mathrm{vN}}(t) = -\mathrm{Tr}\left[\hat{\rho}^{(\mathrm{old})}(t) \ln \hat{\rho}^{(\mathrm{old})}(t)\right] \\ \underbrace{= S^{(\mathrm{old})}_{\mathrm{vN}}(0) = -\mathrm{Tr}\left[\hat{\rho}(0) \ln \hat{\rho}(0)\right]}_{\substack{\text{old entropy did not change} \\ \text{because } p_{\alpha\alpha'}\text{'s did not change}}}. \tag{13.30}$$

So information is lost and we move forward to an ever more boring world... (which is a very interesting fact, so don't despair!)

You might think of what has happened as *our total ignorance about the environment having polluted our knowledge about the system as a result of the latter getting entangled with the former.*

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# PART IV
# Statistical Mechanics of Simple Systems

*This part of the course was taught, in succession, by Professors Andrew Boothroyd, Julien Devriendt (2021), and Andrew Steane.*

# PART V
# Open Systems

## 14. Grand Canonical Ensemble

So you know what to do if you are interested in a system whose quantum states you know and whose probabilities of being in any one of these states you have to guess based on (the expectation of) the knowledge of some measurable mean quantities associated with the system. So far (except in §10.4) the measurable quantity has always been mean energy—and the resulting canonical distribution gave a good statistical description of a physical system in contact with a heat bath at some fixed temperature.

Besides the measurable mean energy $U$, our system depended on a number of *exactly fixed external parameters:* the volume $V$, the number of particles $N$—these were not constraints, they did not need to be measured, they were just there, set in stone (a box of definite volume, with impenetrable walls, containing a definite, exact number of particles). Mathematically speaking, the microstates of the system depended parametrically on $V$ and $N$ and so did their energies:[62]

$$\alpha = \alpha(V, N), \quad E_\alpha = E_\alpha(V, N). \tag{14.1}$$

There are good reasons to recast $N$ as a measurable mean quantity rather than a fixed parameter. This will allow us to treat systems that are not entirely closed and so can exchange particles with other systems. For example:

---

[62] E.g., for ideal gas, $\alpha$ depended on $V$ via the set of possible values of particles' momenta (11.3) and on $N$ via the fixed sum of the occupation numbers (11.22).

—inhomogeneous systems in some external potential (gravity, electric field, rotation, etc.), in which parts of the system can be thought of as exchanging particles with other parts where the external potential has a different value (§14.5);

—multiphase systems, where different phases (e.g., gaseous, liquid, solid) can exchange particles via evaporation, condensation, sublimation, solidification, etc. (§15.2, Part VII);

—systems containing different substances that can react with each other and turn into each other (§15), e.g., chemical reacting mixtures (§§15.3 and 15.4), partially ionised plasmas subject to ionisation/recombination (Exercise 15.3);

—systems in which the number of particles is not fixed at all and is determined by the requirements of thermodynamical equilibrium, e.g., pair production/annihilation (Exercise 16.7), thermal radiation (§19), etc.;

—systems where $N$ might be fixed, but, for greater ease of counting microstates, it is convenient formally to allow it to vary (Fermi and Bose statistics for quantum gases, §16).

### 14.1. *Grand Canonical Distribution*

We now declare that each microstate $\alpha$ has a certain energy and a certain number of particles associated with it,[63]

$$\alpha \to E_\alpha, N_\alpha, \tag{14.2}$$

and there are two constraints:

$$\sum_\alpha p_\alpha E_\alpha = U \quad \text{mean energy}, \tag{14.3}$$

$$\sum_\alpha p_\alpha N_\alpha = \bar{N} \quad \text{mean number of particles.} \tag{14.4}$$

Both $U$ and $\bar{N}$ are measurable; measuring $\bar{N}$ is equivalent to measuring the *mean particle density*

$$n = \frac{\bar{N}}{V}, \tag{14.5}$$

where $V$ remains an exactly fixed external parameter.

You know the routine: maximise entropy subject to these two constraints:

$$S_\mathrm{G} - \lambda\left(\sum_\alpha p_\alpha - 1\right) - \beta\left(\sum_\alpha p_\alpha E_\alpha - U\right) + \beta\mu\left(\sum_\alpha p_\alpha N_\alpha - \bar{N}\right) \to \max, \tag{14.6}$$

where $-\beta\mu$ is the new Lagrange multiplier responsible for enforcing the new constraint (14.4); the factor of $-\beta$ is introduced to follow the conventional definition of $\mu$, which is called the *chemical potential* and whose physical meaning will shortly emerge. Carrying out the maximisation in the same manner as in §9.1, we find

$$\ln p_\alpha + 1 + \lambda + \beta E_\alpha - \beta\mu N_\alpha = 0. \tag{14.7}$$

[63]There is no complicated meaning to $N_\alpha$: we simply allow states with 1 particle, states with 2 particles, states with 3 particles, . . . , states with $N$ particles, . . . , all to be part of our enlarged set of allowed microstates. Volume is still a parameter, on which both $E_\alpha$ and other quantum numbers may depend, but $N_\alpha$ is not a function of $V$: we always consider states with different values of $N_\alpha$ as different states. Obviously, different states will have different probabilities and so certain values of $N_\alpha$ will be more probable than others, so the *mean* number of particles $\bar{N}$ *will* depend on $V$.

This gives us the *grand canonical distribution:*

$$\boxed{p_\alpha = \frac{e^{-\beta(E_\alpha - \mu N_\alpha)}}{\mathcal{Z}(\beta,\mu)}}, \tag{14.8}$$

where the normalisation factor (arising from the Lagrange multiplier $\lambda$) is the *grand partition function:*

$$\boxed{\mathcal{Z}(\beta,\mu) = \sum_\alpha e^{-\beta(E_\alpha - \mu N_\alpha)}}. \tag{14.9}$$

It remains to calculate $\beta$ and $\mu$. Since

$$\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{1}{\mathcal{Z}} \sum_\alpha (-E_\alpha + \mu N_\alpha) e^{-\beta(E_\alpha - \mu N_\alpha)} = -U + \mu \bar{N}, \tag{14.10}$$

the first implicit equation for $\beta$ and $\mu$ in terms of $U$ and $\bar{N}$ is

$$U(\beta,\mu) = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \mu \bar{N}(\beta,\mu). \tag{14.11}$$

The second equation arises from noticing that

$$\frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{1}{\mathcal{Z}} \sum_\alpha \beta N_\alpha e^{-\beta(E_\alpha - \mu N_\alpha)} = \beta \bar{N}, \tag{14.12}$$

and so

$$\bar{N}(\beta,\mu) = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}. \tag{14.13}$$

---

Note that the canonical distribution and the canonical partition function (§9.1) can be recovered as a special case of our new theory: suppose that for all $\alpha$, the number of particles is the same,

$$N_\alpha = N \quad \text{for all } \alpha. \tag{14.14}$$

Then (14.8) becomes

$$p_\alpha = e^{-\beta E_\alpha} \underbrace{\frac{e^{\beta\mu N}}{\mathcal{Z}}}_{=1/Z} = \frac{e^{-\beta E_\alpha}}{Z}, \tag{14.15}$$

which is our old canonical distribution (9.8), where, using (14.9),

$$Z = e^{-\beta\mu N} \mathcal{Z} = e^{-\cancel{\beta\mu N}} \sum_\alpha e^{-\beta(E_\alpha - \cancel{\mu N})} = \sum_\alpha e^{-\beta E_\alpha} \tag{14.16}$$

is the familiar non-grand partition function (9.7). The relationship between the grand and non-grand partition functions, when written in the form

$$\mathcal{Z} = (e^{\beta\mu})^N Z(\beta), \tag{14.17}$$

highlights a quantity sometimes referred to as "fugacity" $\equiv e^{\beta\mu}$.

---

### 14.2. *Thermodynamics of Open Systems and the Meaning of Chemical Potential*

We are now ready to generalise the construction of thermodynamics from §9.2 to the case of open systems.

The Gibbs entropy in the grand canonical equilibrium is

$$S_G = -\sum_\alpha p_\alpha \ln p_\alpha = -\sum_\alpha p_\alpha \left[-\beta(E_\alpha - \mu N_\alpha) - \ln \mathcal{Z}\right] = \beta(U - \mu \bar{N}) + \ln \mathcal{Z}. \tag{14.18}$$

Its differential is

$$
\begin{aligned}
\mathrm{d}S_{\mathrm{G}} &= \beta(\mathrm{d}U - \bar{N}\mathrm{d}\mu - \mu\mathrm{d}\bar{N}) + (U - \mu\bar{N})\mathrm{d}\beta + \frac{\mathrm{d}\mathcal{Z}}{\mathcal{Z}} \\
&= \beta(\mathrm{d}U - \cancel{\bar{N}\mathrm{d}\mu} - \mu\mathrm{d}\bar{N}) + \cancel{(U - \mu\bar{N})\mathrm{d}\beta} \\
&\quad + \sum_\alpha \underbrace{\frac{e^{-\beta(E_\alpha - \mu N_\alpha)}}{\mathcal{Z}}}_{=\,p_\alpha} \left[-\beta(\mathrm{d}E_\alpha - \cancel{N_\alpha \mathrm{d}\mu}) - \cancel{(E_\alpha - \mu N_\alpha)\mathrm{d}\beta}\right] \\
&= \beta\Bigg(\mathrm{d}U - \mu\mathrm{d}\bar{N} - \underbrace{\sum_\alpha p_\alpha \mathrm{d}E_\alpha}_{=\left\langle \frac{\partial E_\alpha}{\partial V}\right\rangle \mathrm{d}V}\Bigg) \\
&= \beta\left(\mathrm{d}U + P\mathrm{d}V - \mu\mathrm{d}\bar{N}\right) = \beta\mathrm{d}Q_{\mathrm{rev}}.
\end{aligned}
\tag{14.19}
$$

We have taken $E_\alpha = E_\alpha(V)$ (energy levels are a function of the single remaining external parameter $V$, the volume of the system) but $\mathrm{d}N_\alpha = 0$ ($N_\alpha$ is not a function of $V$; see footnote 63 in §14.1); we have also used our standard definition of pressure (7.13).

The right-hand side of (14.19) has to be identified as $\beta\mathrm{d}Q_{\mathrm{rev}}$ because we would like to keep the correspondences between $S_{\mathrm{G}}$ and the thermodynamical entropy (9.14) and between $\beta$ and the thermodynamical temperature (9.13):

$$
S_{\mathrm{G}} = \frac{S}{k_{\mathrm{B}}}, \quad \beta = \frac{1}{k_{\mathrm{B}}T}. \tag{14.20}
$$

This implies the physical interpretation of $\mu$: *in a reversible process where $U$ and $V$ stay the same but $\bar{N}$ changes, adding each particle generates $-\mu$ amount of heat.* In other words,

$$
\boxed{\mu = -T\left(\frac{\partial S}{\partial \bar{N}}\right)_{U,V}}\,. \tag{14.21}
$$

Intuitively, adding particles should increase entropy (systems with more particles usually have a larger number of microstates available to them, so the uncertainty as to which of these microstates they are in is likely to be greater)—therefore, we expect $\mu$ to be a negative quantity, under normal circumstances. Equivalently, one might argue that a positive value of $\mu$ would imply that entropy increased with diminishing $\bar{N}$ and so, in its quest to maximise entropy, a system with positive $\mu$ would be motivated to lose all its particles and thus cease to be a system. This logic is mostly correct, although we will encounter an interesting exception in the case of degenerate Fermi gas (§17).

We are now ready to write the *fundamental equation of thermodynamics of open systems*, generalising (9.15):

$$
\boxed{\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}\bar{N}}\,. \tag{14.22}
$$

Writing it in this form highlights another interpretation of the chemical potential:

$$
\mu = \left(\frac{\partial U}{\partial \bar{N}}\right)_{S,V}, \tag{14.23}
$$

the energy cost of a particle to a system at constant volume and entropy.

---

It is in fact possible to derive (14.19) and the resulting variable-particle-number thermodynamics from the canonical ensemble. Go back to (9.11) and treat the number of particles $N$ as a variable *parameter*, in the same way as volume was treated. Then

$$\sum_\alpha p_\alpha \mathrm{d}E_\alpha = \left\langle \frac{\partial E_\alpha}{\partial V} \right\rangle \mathrm{d}V + \left\langle \frac{\partial E_\alpha}{\partial N} \right\rangle \mathrm{d}N = -P\mathrm{d}V + \mu \mathrm{d}N, \tag{14.24}$$

where I used the definition (7.13) of pressure and introduced the chemical potential in an analogous way as being, *by definition*,

$$\mu = \sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial N} = \left\langle \frac{\partial E_\alpha}{\partial N} \right\rangle, \tag{14.25}$$

where $p_\alpha$ are the *canonical* probabilities (9.8). In this scheme, $\mu$ is explicitly *defined* as the energy cost of an extra particle [cf. (14.23)], in the same way that $-P$ is the energy cost of an extra piece of volume.

This illustrates that, in constructing various ensembles, we have some degree of choice as to which quantities we treat as measurable constraints ($U$ in the canonical ensemble, $U$ and $\bar{N}$ in the grand canonical one) and which as exactly fixed external parameters that can be varied between different equilibria ($V$ in the grand canonical ensemble, $V$ and $N$ in the version of the canonical ensemble that I have just outlined). In Exercise 14.7, this point is further illustrated with an ensemble in which volume becomes a measurable constraint and pressure the corresponding Lagrange multiplier.

---

To complete our new thermodynamics, let us generalise the concept of free energy: using (14.18) and (14.20), we introduce a new thermodynamical quantity

$$\boxed{\Phi = -k_{\mathrm{B}} T \ln \mathcal{Z} = U - TS - \mu \bar{N} = F - \mu \bar{N}}\,, \tag{14.26}$$

called the *grand potential* (its physical meaning will become clear in §14.6.3). The usefulness of this quantity for open systems is the same as the usefulness of $F$ for closed ones: it is the function by differentiating which one gets all the relevant thermodynamical quantities and equations. Indeed, using (14.22), we get

$$\boxed{\mathrm{d}\Phi = -S\mathrm{d}T - P\mathrm{d}V - \bar{N}\mathrm{d}\mu}\,, \tag{14.27}$$

and so,

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}, \tag{14.28}$$

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \quad \left(\text{equivalently, equation for density } n = \frac{\bar{N}}{V}\right), \tag{14.29}$$

$$U = \Phi + TS + \mu \bar{N}, \tag{14.30}$$

$$P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}, \quad \text{equation of state} \tag{14.31}$$

(note that the equation of state will, in fact, turn out to be obtainable in an even simpler way than this: see §14.6.3).

Similarly to the case of fixed number of particles, we have found that all we need to do, pragmatically, is calculate the (grand) partition function $\mathcal{Z}(\beta, \mu)$, which incorporates all the microphysics relevant to the thermodynamical description, infer from it the grand potential $\Phi$, and then take derivatives of it—and we get to know everything we care about.

<u>What is the role that $\mu$ plays in all this?</u> Equation (14.22) suggests that $-\mu$ to $\bar{N}$ is what $P$ is to $V$ or $1/T$ to $U$, i.e., it regulates the way in which some form of equilibrium is achieved across a system.

## 14.3. *Particle Equilibrium*

Similarly to what we did in §10.2, consider two systems in thermal and particle contact (i.e., capable of exchanging energy and matter), but otherwise isolated. The name of the game is to maximise entropy subject to conserved total (mean) energy and particle number:

$$U = U_1 + U_2 = \text{const}, \tag{14.32}$$
$$\bar{N} = \bar{N}_1 + \bar{N}_2 = \text{const}, \tag{14.33}$$
$$S = S_1 + S_2 \to \max. \tag{14.34}$$

Taking differentials (between equilibrium states),

$$\begin{aligned} \mathrm{d}S &= \left(\frac{\partial S_1}{\partial U_1}\right)_{\bar{N}_1,V_1} \mathrm{d}U_1 + \left(\frac{\partial S_1}{\partial \bar{N}_1}\right)_{U_1,V_1} \mathrm{d}\bar{N}_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{\bar{N}_2,V_2} \underbrace{\mathrm{d}U_2}_{=-\mathrm{d}U_1} + \left(\frac{\partial S_2}{\partial \bar{N}_2}\right)_{U_2,V_2} \underbrace{\mathrm{d}\bar{N}_2}_{=-\mathrm{d}\bar{N}_1} \\ &= \underbrace{\left[\left(\frac{\partial S_1}{\partial U_1}\right)_{\bar{N}_1,V_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{\bar{N}_2,V_2}\right]}_{=\frac{1}{T_1}-\frac{1}{T_2}} \mathrm{d}U_1 + \underbrace{\left[\left(\frac{\partial S_1}{\partial \bar{N}_1}\right)_{U_1,V_1} - \left(\frac{\partial S_2}{\partial \bar{N}_2}\right)_{U_2,V_2}\right]}_{=-\frac{\mu_1}{T_1}+\frac{\mu_2}{T_2}} \mathrm{d}\bar{N}_1 = 0, \end{aligned} \tag{14.35}$$

where we have used (14.21) to identify the derivatives in the second term. Setting the first term to zero gives $T_1 = T_2 = T$ (thermal equilibrium). Then setting the second term to zero implies that

$$\boxed{\mu_1 = \mu_2}\,, \tag{14.36}$$

i.e., $\mu = \text{const}$ *across a system in equilibrium.* We also see that, if initially $\mu_1 \neq \mu_2$, the direction of change, set by $\mathrm{d}S > 0$, is $\mu_1 < \mu_2 \Leftrightarrow \mathrm{d}\bar{N}_1 > 0$, so *matter flows from larger to smaller* $\mu$.

Thus, if we figure out how to calculate $\mu$, we should be able to predict equilibrium states: how many particles, on average, there will be in each part of a system in equilibrium.

*NB:* Let me reiterate the point that has (implicitly) been made in several places before. Extensive thermodynamic variables like $U$, $V$, $\bar{N}$ have intensive *conjugate variables* associated with them: $1/T$, $P/T$, $-\mu/T$. They represent "entropic" costs of changing the extensive variables; equivalently, $T$, $-P$ and $\mu$ are energetic costs of changing the system's entropy, volume and particle number, respectively [see (14.22)]. It turns out that these costs cannot vary across the free-trade zone that a system in equilibrium is.

---

**Exercise 14.1. Microcanonical Ensemble Revisited.** Derive the grand canonical distribution starting from the microcanonical distribution (i.e., by considering a small subsystem exchanging particles and energy with a large, otherwise isolated system). This is a generalisation of the derivation in §12.1.2.

---

## 14.4. *Grand Partition Function and Chemical Potential of Classical Ideal Gas*

So let us then learn how to calculate $\mu$ for our favourite special case of a classical monatomic ideal gas.

As always, the key question is what are the microstates? The answer is that they are the same as before [see (11.22)], except now we can have an arbitrary number of particles, so

$$\alpha = \{\alpha_N, N\}, \tag{14.37}$$

where

$$\alpha_N = \{n_{\boldsymbol{k}_1}, n_{\boldsymbol{k}_2}, \dots\}, \quad \sum_{\boldsymbol{k}} n_{\boldsymbol{k}} = N, \tag{14.38}$$

are the microstates of a gas of $N$ particles and $n_{\boldsymbol{k}}$ are occupation numbers of the single-particle states designated by the wave vectors $\boldsymbol{k}$.

The grand partition function is, therefore,

$$\mathcal{Z} = \sum_\alpha e^{-\beta(E_\alpha - \mu N_\alpha)} = \sum_N e^{\beta\mu N} \sum_{\alpha_N} e^{-\beta E_{\alpha_N}} = \sum_N e^{\beta\mu N} Z_N, \tag{14.39}$$

where $Z_N$ is the familiar partition function of a gas of $N$ particles, for which, neglecting quantum correlations, we may use (11.26):

$$\mathcal{Z} \approx \sum_N e^{\beta\mu N} \frac{Z_1^N}{N!} = \sum_N \frac{(e^{\beta\mu} Z_1)^N}{N!} = e^{Z_1 e^{\beta\mu}}. \tag{14.40}$$

The grand potential (14.26) is, therefore,

$$\Phi = -k_{\rm B} T \ln \mathcal{Z} = -k_{\rm B} T Z_1 e^{\mu/k_{\rm B}T}. \tag{14.41}$$

Using (14.29),

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = Z_1 e^{\mu/k_{\rm B}T}, \tag{14.42}$$

whence

$$\boxed{\mu = -k_{\rm B} T \ln \frac{Z_1}{\bar{N}}}\,. \tag{14.43}$$

Now recall that the single-particle partition function is

$$Z_1 = \frac{V}{\lambda_{\rm th}^3} Z_1^{(\rm internal)}, \quad \lambda_{\rm th} = \hbar\sqrt{\frac{2\pi}{m k_{\rm B} T}}, \tag{14.44}$$

where the first factor is the single-particle partition function associated with the particles' translational degrees of freedom and $Z_1^{(\rm internal)}$ is the partition function associated with whatever internal degrees of freedom the particles have, e.g., for a diatomic gas,

$$Z_1^{(\rm internal)} = Z_1^{(\rm rotational)} Z_1^{(\rm vibrational)}. \tag{14.45}$$

The chemical potential (14.43) is then

$$\boxed{\mu = k_{\rm B} T \ln \frac{n\lambda_{\rm th}^3}{Z_1^{(\rm internal)}}}\,, \tag{14.46}$$

where $n = \bar{N}/V$ is the (mean) number density of the gas. Note that, as $n\lambda_{\rm th}^3 \ll 1$ in the classical limit [see (11.30)] and $Z_1^{(\rm internal)} \geqslant 1$ (because the number of internal states is at least 1), the formula (14.46) gives $\mu < 0$, as anticipated in §14.2.

Finally, using (14.40–14.42), we get two remarkably simple formulae:

$$\mathcal{Z} = e^{\bar{N}}, \tag{14.47}$$

$$\Phi = -k_{\rm B} T \bar{N}, \tag{14.48}$$

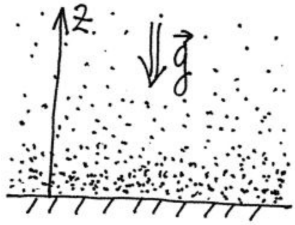


FIGURE 24. A stratified atmosphere.

whence the free energy is [see (14.26)]

$$F = \Phi + \mu\bar{N} = -k_B T\bar{N}\left(1 - \ln\frac{n\lambda_{th}^3}{Z_1^{(\text{internal})}}\right). \qquad (14.49)$$

Comparing this with the expression (11.32) that we previously had for the free energy of ideal gas, we see that it has not changed, except for $N$ having been replaced by $\bar{N}$ (and the appearance of $Z_1^{(\text{internal})}$, which we did not yet know about in §11.10). This means that *all our results previously derived for the case of a fixed number of particles survive, with* $N \to \bar{N}$.

**Exercise 14.2. Particle Number Distribution.** Consider a volume $V$ of classical ideal gas with mean number density $n = \bar{N}/V$, where $\bar{N}$ is the mean number of particles in this volume. Starting from the grand canonical distribution, show that the probability to find exactly $N$ particles in this volume is a Poisson distribution (thus, you will recover by a different method the result of Exercise 1.2a).

### 14.5. *Equilibria of Inhomogeneous Systems*

Let us now learn how to calculate the equilibrium states of a class of systems embedded in some external space-dependent potential $\varphi(\boldsymbol{r})$. For example, consider a classical ideal gas in a uniform gravitational field (an *atmosphere*; Fig. 24), i.e., in a potential

$$\varphi(z) = gz. \qquad (14.50)$$

If this system is in equilibrium, we know (§14.3) that both $T$ and $\mu$ must be the same everywhere in it (think of subdividing the atmosphere into thin layers of constant $z$ and requiring them all to be equilibrated with each other). So, we have

$$T(z) = \text{const} \qquad (14.51)$$

(an isothermal atmosphere is obviously not a great model of the real thing, but this is not the point right now; see Exercise 14.5 for a more realistic model of our atmosphere). Using (14.43),

$$\mu(z) = -k_B T \ln\frac{Z_1}{\bar{N}} = \text{const}. \qquad (14.52)$$

The single-particle energy levels are the same as before plus potential energy per particle, $m\varphi = mgz$. In other words, $Z_1^{(\text{internal})}$ in (14.44) contains a factor corresponding to the gravitational energy level (there is only one):

$$Z_1^{(\text{grav})} = e^{-\beta mgz}. \qquad (14.53)$$

Therefore,

$$Z_1 = Z_1(g=0)Z_1^{(\text{grav})} = Z_1(g=0)e^{-\beta mgz}, \qquad (14.54)$$

where $Z_1(g=0)$ is the single-particle partition function for a gas at zero gravity. Then (14.52) becomes

$$\mu = \mu(g=0) + mgz = k_B T \ln \frac{n(z)\lambda_{th}^3}{Z_1^{(internal)}} + mgz = \text{const}, \tag{14.55}$$

where I have used (14.46) for $\mu(g=0)$, the chemical potential of ideal gas at zero gravity. The only way for a $z$ dependence to enter in the first term in (14.55) is via the particle density $n$ because $T = \text{const}$ in equilibrium. We find, therefore, a density profile known as the *Boltzmann distribution* (or *Boltzmann response*):

$$\boxed{n(z) = n(0)e^{-mgz/k_B T}}, \tag{14.56}$$

where $n(0)$ is the density at $z = 0$.

The obvious generalisation of this result for a system in a general potential is

$$n(\boldsymbol{r}) \propto e^{-w(\boldsymbol{r})/k_B T}, \tag{14.57}$$

where $w(\boldsymbol{r})$ is the potential energy per particle at location $\boldsymbol{r}$ (obviously, it must be assumed that that $w(\boldsymbol{r})$ varies at characteristic distances long enough for the quantum uncertainty as to the particle positions not to matter, i.e., effectively, at every $\boldsymbol{r}$ there is a little homogeneous box).

Remark. An interesting and useful formal lesson from (14.55) is that if we know the single-particle behaviour of some system and wish to adapt this knowledge to the same system but with energy levels shifted by some amount $w$, all we need to do is replace

$$\mu \to \mu + w \tag{14.58}$$

everywhere (this trick can be used, e.g., in the treatment of magnetisation; see Exercises 17.5 and 18.3). This makes sense: $\mu$ is the energy cost of adding a particle to the system [see (14.23)], so it has to shift by $w$ if particles have additional energy $w$.

Remark. It is not hard to grasp the dynamical origin of (14.56). Clearly, there is a downward pressure gradient in the atmosphere. This will exert a force [see (6.21)]. In a static ($\boldsymbol{u} = 0$) equilibrium, this force must be compensated by something—obviously, gravity, so

$$-\frac{\partial P}{\partial z} - mng = 0 \tag{14.59}$$

(this is called a *hydrostatic equlibrium*). Letting $P = nk_B T$ and assuming $T = \text{const}$, we get a differential equation for $n(z)$, whose solution is the Boltzmann distribution (14.56).

---

**Exercise 14.3. Rotating Gas.** (a) A cylindrical container of radius $R$ is filled with ideal gas at temperature $T$ and rotating around the axis with angular velocity $\Omega$. The molecular mass is $m$. The mean density of the gas without rotation is $\bar{n}$. Assuming the gas is in isothermal equilibrium, what is the gas density at the edge of the cylinder, $n(R)$? Discuss the high and low temperature limits of your result.

(b) Putting a mixture of two gases with different particle masses into a rotating container (a *centrifuge*) is a way to separate heavier from lighter particles (e.g., separate isotopes). Another method of doing this was via effusion (see comment at the end of §3). Making a set of sensible assumptions about all the parameters you need, assess the relative merits of the two methods.

(c) In the calculation of the "isothermal atmosphere" we imagined subdividing it into thin horizontal layers, each at constant $z$, and treated each layer as a homogeneous system. Similarly, here, you had to imagine subdividing the cylinder into thin annular layers, each at constant radius. Why can we use for this system the results originally derived in a rectangular box (from §11.1 onwards)? Does it matter that we might not be describing quite correctly the particles with low wave numbers (say, $k \sim R^{-1}$)?

**Exercise 14.4. Debye Screening.** (a) Consider a charged plate kept at the potential $\varphi_0$ and bounding a semi-infinite hydrogen plasma (an ideal gas consisting of ions and electrons with charges $e$ and $-e$, respectively). Assume that the plasma is in isothermal equilibrium with temperature $k_{\rm B}T \gg e\varphi_0$. The electrostatic potential satisfies Gauss's law:

$$-\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2} = 4\pi e[n_i(x) - n_e(x)], \tag{14.60}$$

where $x$ is the distance from the plate and $n_i$ and $n_e$ are number densities of ions and electrons, respectively. Assume that at $x \to \infty$, $\varphi \to 0$, and the number densities of ions and electrons are equal: $n_{i,e} \to n_\infty = \mathrm{const}$ (i.e., the plasma is neutral). Show that

$$\varphi(x) = \varphi_0 e^{-x/\lambda_{\rm D}}, \quad \text{where} \quad \lambda_{\rm D} = \sqrt{\frac{k_{\rm B}T}{8\pi e^2 n_\infty}}. \tag{14.61}$$

Thus, plasma screens (or shields) the plate's charge over a typical distance $\lambda_{\rm D}$, known as the *Debye length.*

(b) The same mechanism is responsible for charges of all particles in a plasma being screened. Considering, for example, a charged hydrogen ion in an infinite homogeneous isothermal hydrogen plasma, and using the same logic as above, show that the ion's potential as a function of distance $r$ from the ion's location is

$$\varphi(r) = \frac{e}{r}\, e^{-r/\lambda_{\rm D}}, \tag{14.62}$$

i.e., that individual charged particles cannot "see" each other's Coulomb potential behind the crowd of other particles beyond distances $\sim \lambda_{\rm D}$.

**Exercise 14.5. Adiabatic Atmosphere.** Obviously, we know that our atmosphere is not isothermal: it gets really cold high up there (as airplane stowaways learn to their chagrin). Can we come up with a better model? The reason atmosphere is not isothermal is that air is, in fact, a poor conductor of heat, so the natural assumption is that, as parcels of air move around, they do not exchange heat with their surroundings and so their entropy remains the same. Indeed, recall what you learned in Exercise 11.3: in the absence of (collisional) heat and momentum exchange, specific entropy is simply carried around by the flow of the gas—the gas moves *adiabatically.* Now imagine that parcels of air move around and eventually settle in such a way that their temperature and pressure are functions only of the height $z$. Since this atmosphere is a result of adiabatic rearrangements and since it is (we assume) thoroughly mixed, we expect that the specific entropy and, therefore, the quantity $Pn^{-5/3}$ is constant everywhere. The result that we proved in Exercise 11.3 was for a monatomic gas, hence the adiabatic index 5/3, but it is not hard to convince onself that it is also true for a more general gas with 5/3 replaced by the general adibatic index $\gamma = C_P/C_V$.

(a) Assume that $Pn^{-\gamma} = \mathrm{const}$ and use this equation in combination with the ideal-gas equation of state and the force balance (14.59) to derive a differential equation for $T(z)$. Show that its solution is

$$T(z) = T_0\left(1 - \frac{\gamma-1}{\gamma}\frac{mg}{k_{\rm B}T_0}\, z\right), \tag{14.63}$$

where $T_0$ is the temperature at the ground level. Hence work out the pressure and density profiles of an adiabatic atmosphere.

(b) Estimate the characteristic height of the Earth's atmosphere (answer: $\sim 30$ km).

(c) Examining your solution, do you expect it to be valid all the way to $z \to \infty$? It should be mathematically obvious to you that the answer to this question is no; the physical reason is that beyond a certain height, the air is no longer strongly mixed and the adiabatic law ceases to apply—you are in a position to speculate, or find out, why that might be so.

## 14.6. *Chemical Potential and Thermodynamic Potentials*

Finally, let us derive a few important general results concerning the relationship between $\mu$ and various thermodynamical quantities.

### 14.6.1. *Free Energy*

Using (14.26) and (14.27), we find that

$$\boxed{\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}\bar{N}}\,, \tag{14.64}$$

a generalisation of (7.2) to open systems. Hence the chemical potential is

$$\mu = \left(\frac{\partial F}{\partial \bar{N}}\right)_{T,V}, \tag{14.65}$$

free energy per particle in systems with fixed temperature and volume.

### 14.6.2. *Gibbs Free Energy*

By the same token, Gibbs free energy, $G = U - TS + PV = F + PV$, satisfies

$$\boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}\bar{N}}\,, \tag{14.66}$$

and so the chemical potential is

$$\mu = \left(\frac{\partial G}{\partial \bar{N}}\right)_{T,P}, \tag{14.67}$$

Gibbs free energy per particle in systems with fixed temperature and pressure.

This result leads to a remarkable further simplification. Since $G = G(P, T, \bar{N})$ is an extensive quantity, $P$ and $T$ are intensive and $\bar{N}$ extensive, if we change $\bar{N}$ by a factor of $\lambda$, $G$ must change by the same factor while $P$ and $T$ stay the same:

$$G(P, T, \lambda\bar{N}) = \lambda G(P, T, \bar{N}). \tag{14.68}$$

Differentiate this with respect to $\lambda$, then set $\lambda = 1$:

$$\left(\frac{\partial G}{\partial(\lambda\bar{N})}\right)_{P,T}\bar{N} = G, \quad \lambda = 1 \quad \Rightarrow \quad \underbrace{\left(\frac{\partial G}{\partial \bar{N}}\right)_{P,T}}_{\substack{=\,\mu,\\ \text{see (14.67)}}}\bar{N} = G. \tag{14.69}$$

We have discovered that

$$\boxed{\mu = \frac{G}{\bar{N}}}\,, \tag{14.70}$$

i.e., *chemical potential is simply Gibbs-free-energy density!*

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**Exercise 14.6.** Calculate $G = U - TS + PV$ for the ideal gas using the results of §11.10 and compare the outcome with (14.46).

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The formula (14.70) implies that $\mu$ *is an intensive quantity* (this was, of course, already obvious) and so

$$\forall\lambda, \quad \mu(P, T, \lambda\bar{N}) = \mu(P, T, \bar{N}) \quad \Rightarrow \quad \mu = \mu(P, T), \tag{14.71}$$

*chemical potential is a function of pressure and temperature only.* Indeed, for the ideal gas, using $P = nk_BT$, the expression (14.46) for the chemical potential becomes

$$\mu = k_BT\ln\frac{n\lambda_{th}^3}{Z_1^{(\text{internal})}} = k_BT\ln P + \underbrace{k_BT\ln\frac{\lambda_{th}^3}{k_BTZ_1^{(\text{internal})}}}_{\text{function of } T \text{ only}}. \tag{14.72}$$

14.6.3. *Meaning of Grand Potential*

Using (14.70),

$$\Phi = F - \mu\bar{N} = F - G = -PV. \tag{14.73}$$

This implies that knowing $\Phi$ instantly gives us the equation of state:

$$\boxed{P = -\frac{\Phi}{V}}, \tag{14.74}$$

a simpler formula than (14.31), as promised at the end of §14.2 [this works really well for ideal gas: see (14.48)]. This result tells us that *pressure is minus the grand-potential density*, a way to give physical meaning to the thus far formal quantity $\Phi$.

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**Exercise 14.7. Pressure Ensemble.** Throughout this course, we have repeatedly discussed systems whose volume is not fixed, but allowed to come to some equilibrium value under pressure. Yet, in both canonical (§9) and grand canonical (§14) ensembles, we treated volume as an external parameter, not as a quantity only measurable in the mean. In this Exercise, your objective is to construct an ensemble in which the volume is not fixed.

(a) Consider a system with (discrete) microstates $\alpha$ to each of which corresponds some energy $E_\alpha$ and some volume $V_\alpha$. Maximise the Gibbs entropy subject to the measured mean energy being $U$ and the mean volume $\bar{V}$, with the number of particles $N$ exactly fixed, and find the probabilities $p_\alpha$. Show that the ("grandish") partition function for this ensemble can be defined as

$$\mathcal{Z} = \sum_\alpha e^{-\beta E_\alpha - \sigma V_\alpha}, \tag{14.75}$$

where $\beta$ and $\sigma$ are Lagrange multipliers. How are $\beta$ and $\sigma$ calculated?

(b) Show that if we demand that the Gibbs entropy $S_G$ for those probabilities be equal to $S/k_B$, where $S$ is the thermodynamic entropy, then the Lagrange multiplier arising from the mean-volume constraint is

$$\sigma = \beta P = \frac{P}{k_BT}, \tag{14.76}$$

where $P$ is pressure. Thus, this ensemble describes a system under pressure set by the environment.

(c) Prove that

$$dU = TdS - Pd\bar{V}. \tag{14.77}$$

(d) Show that

$$-k_BT\ln\mathcal{Z} = G, \tag{14.78}$$

where $G$ is the Gibbs free energy defined in the usual way. How does one derive the equation of state for this ensemble?

(e) Calculate the partition function $\mathcal{Z}$ for a classical monatomic ideal gas in a container of changeable volume but impermeable to particles (e.g., a balloon made of inelastic material). You will find it useful to consider microstates of an ideal gas at fixed volume $V$ and then sum up over all possible values of $V$. This sum (assumed discrete) can be converted to an integral via $\sum_V = \int_0^\infty dV/\Delta V$, where $\Delta V$ is the "quantum of volume" (an artificial quantity shortly to be eliminated from the theory; how small must $\Delta V$ be in order for the sum and the integral to be good approximations of each other?). *Hint.* You will need to use the formula $\int_0^\infty dx\, x^N e^{-x} = N!$

(f) Calculate $G$ and find what conditions $\Delta V$ must satisfy in order for the resulting expression to coincide with the standard formula for the ideal gas (derived in Exercise 14.6) and be independent of $\Delta V$ (assume $N \gg 1$). If you can argue that the unphysical quantity $\Delta V$ does not affect any physically testable results, then your theory is sensible.

(g) Show that the equation of state is

$$P = nk_{\mathrm{B}}T, \quad n = \frac{N}{\bar{V}}. \tag{14.79}$$

[cf. Lewis & Siegert 1956]

**Exercise 14.8. Expansio ad absurdum.** Try constructing the "grandiose" ensemble, where all three of mean energy, mean volume and mean number of particles are treated as measurable constraints. Why is such a theory impossible/meaningless?

**Exercise 14.9. Statistical Mechanics of a Black Hole.** Here we pick up from our earlier digression on the thermodynamics of black holes (see §10.5.1).

Consider the following model of a Schwarzschild black hole's quantum states. Assume that its horizon's area is quantised according to

$$A_n = a_0 n, \quad n = 1, 2, 3, \ldots, \quad a_0 = 4\ell_{\mathrm{P}}^2 \ln k, \quad \ell_{\mathrm{P}} = \sqrt{\frac{G\hbar}{c^3}}, \tag{14.80}$$

where $\ell_{\mathrm{P}}$ is the Planck length and $\ln k$ is some constant. Assume further that there are many equiprobable microstates corresponding to each value of the area and use Bekenstein's entropy (10.40) to guess what the number $\Omega_n$ of such states is:

$$\frac{S_n}{k_{\mathrm{B}}} = \frac{A_n}{4\ell_{\mathrm{P}}^2} = \ln \Omega_n \quad \Rightarrow \quad \Omega_n = k^n. \tag{14.81}$$

Finally, assume that the mass of the black hole corresponding to each value of $A_n$ is given (at least approximately, for black holes much larger than the Planck length) by Schwarzschild's formula (10.38):

$$M_n = m_0\sqrt{n}, \quad m_0 = \frac{c^2}{G}\sqrt{\frac{a_0}{16\pi}} = m_{\mathrm{P}}\sqrt{\frac{\ln k}{4\pi}}, \quad m_{\mathrm{P}} = \sqrt{\frac{\hbar c}{G}}, \tag{14.82}$$

where $m_{\mathrm{P}}$ is the Planck mass.

(a) Assume that the only measurable constraint in the problem is the mean mass of the black hole, $\bar{M} = \langle M_n \rangle$ (equivalently, $\langle\sqrt{n}\rangle$). Use the maximum-entropy principle to calculate probabilities of microstates. Are you able to calculate the partition function? Why not? If you study the literature, you will see that a lot of other people have grappled with the same problem, some less convincingly than others.

(b) Try instead a kind of "grand canonical" approach, applying the maximum-entropy principle with two constraints: the mean area of the horizon $\bar{A} = \langle A_n \rangle$ (equivalently, $\langle n \rangle$) and the mean mass $\bar{M} = \langle M_n \rangle$. Why is one of the constraints in this scheme not *a priori* superfluous? (I.e., how is this situation different from Exercise 9.1e?)

(c) Show that the resulting partition function is

$$\mathcal{Z} = \sum_n k^n e^{-\mu n + \chi\sqrt{n}}, \tag{14.83}$$

where $\mu$ and $-\chi$ are Lagrange multipliers (one could interpret $\mu$ as a kind of chemical potential). Argue that one can obtain a finite $\mathcal{Z}$ and a black hole with large area and mass (compared with the Planck area and mass) if $\chi \gg \gamma \equiv \mu - \ln k > 0$. Assuming that this is the case, calculate the partition function approximately, by expanding the exponent in (14.83) around the value $n = n_0$ where it is at its maximum. You should find that

$$\mathcal{Z} \approx \sqrt{\frac{4\pi n_0}{\gamma}}\, e^{\gamma n_0}\left[1 + O\left(\frac{1}{\sqrt{\gamma n_0}}\right)\right], \quad n_0 = \left(\frac{\chi}{2\gamma}\right)^2. \tag{14.84}$$

(d) Find expressions for $\bar{A}$ and $\bar{M}$ in terms of $\gamma$ and $n_0$ (or, equivalently, $\gamma$ and $\chi$), keeping the dominant and the largest subdominant terms in the large-$n_0$ expansion. Hence show that $\bar{A}$ and $\bar{M}$ satisfy the Schwarzschild relation (10.38) to lowest order and also that the entropy (calculated for the distribution that you have obtained) and the area $\bar{A}$ satisfy the Bekenstein formula (10.40) in the same limit, up to a logarithmic correction, viz.,

$$\frac{S}{k_{\rm B}} = \frac{\bar{A}}{4\ell_{\rm P}^2} + \frac{1}{2}\ln\frac{\bar{A}}{4\ell_{\rm P}^2} + O(1). \tag{14.85}$$

(e) Confirm that neither of the two constraints that we have imposed is superfluous. However, would any arbitrary values of $\bar{A}$ and $\bar{M}$ lead to valid thermodynamics, with definite values of the Lagrange multipliers obtainable?

(f) Finally, work out the relationship between the entropy and the mean energy ($U = \bar{M}c^2$) and show that the temperature defined by $1/T = {\rm d}S/{\rm d}U$ is the Hawking temperature (10.39). Why is the temperature not just the Lagrange multiplier $-\chi$ and, therefore, negative?

(g) Show that the heat capacity of a black hole is negative and that the mean square fluctuation of the black hole's mass around its mean is

$$\langle (M_n - \bar{M})^2 \rangle = m_{\rm P}^2 \frac{\ln k}{8\pi\gamma}. \tag{14.86}$$

Why is there not a relationship between the heat capacity and the mean square fluctuation of energy (equivalently, mass) analogous to (10.37)?

[cf. Gour 1999]

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## 15. Multi-Species (Multi-Component) Systems

We shall now consider systems containing several different "components": several species of molecules or particles, e.g.,

—solutions,
—mixtures of (reacting) chemicals,
—plasmas (ions + electrons + also neutral atoms if partially ionised).

### 15.1. *Generalisation of the Grand Canonical Formalism to Many Species*

We will characterise the thermodynamic state of a multi-species system by the mean energy $U$ and the mean number of particles $\bar{N}_s$ of each species $s$. Completely analogously to what we did in §14.1, let us maximise $S_{\rm G}$ subject all these quantities being fixed (by measurement)—there will be a Lagrange multiplier for each $s$, so each species will have its own chemical potential $\mu_s$. Leaving the algebra to you as an **exercise**, here are the results (where the equations that these results are generalisations of are indicated):

$$(14.8) \rightarrow \quad p_\alpha = \frac{e^{-\beta(E_\alpha - \sum_s \mu_s N_{s\alpha})}}{\mathcal{Z}}, \tag{15.1}$$

$$(14.9) \rightarrow \quad \mathcal{Z} = \sum_\alpha e^{-\beta(E_\alpha - \sum_s \mu_s N_{s\alpha})}, \tag{15.2}$$

where $N_{s\alpha}$ is the number of particles of species $s$ corresponding to the microstate $\alpha$ of the whole system, and, given $s = 1, \dots, m$ species, the $m+1$ Lagrange multipliers $\beta$, $\mu_1, \dots, \mu_m$ are determined from the following $m+1$ equations:

$$(14.11) \rightarrow \quad U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \sum_s \mu_s \bar{N}_s, \tag{15.3}$$

$$(14.13) \rightarrow \quad \bar{N}_s = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu_s}. \tag{15.4}$$

The grand potential is

$$(14.26) \to \quad \Phi = -k_{\rm B}T\ln\mathcal{Z} = U - TS - \sum_s \mu_s \bar{N}_s, \tag{15.5}$$

$$(14.27) \to \quad {\rm d}\Phi = -S{\rm d}T - P{\rm d}V - \sum_s \bar{N}_s {\rm d}\mu_s, \tag{15.6}$$

and the multispecies thermodynamics, i.e., the expressions for $S$, $\bar{N}_s$, $U$ and $P$, can be read off from this in the same manner as (14.28–14.31) were. The differentials of the thermodynamic potentials (defined in the usual way) are, therefore,

$$(14.22) \to \quad {\rm d}U = T{\rm d}S - P{\rm d}V + \sum_s \mu_s {\rm d}\bar{N}_s, \tag{15.7}$$

$$(14.64) \to \quad {\rm d}F = -S{\rm d}T - P{\rm d}V + \sum_s \mu_s {\rm d}\bar{N}_s, \tag{15.8}$$

$$(14.66) \to \quad {\rm d}G = -S{\rm d}T + V{\rm d}P + \sum_s \mu_s {\rm d}\bar{N}_s, \tag{15.9}$$

whence follow the expressions for the chemical potential of species $s$, analogous to (14.21), (14.23), (14.65) and (14.70):

$$\mu_s = -T\left(\frac{\partial S}{\partial \bar{N}_s}\right)_{U,V,\bar{N}_{s'\neq s}} = \left(\frac{\partial U}{\partial \bar{N}_s}\right)_{S,V,\bar{N}_{s'\neq s}} = \left(\frac{\partial F}{\partial \bar{N}_s}\right)_{T,V,\bar{N}_{s'\neq s}} = \left(\frac{\partial G}{\partial \bar{N}_s}\right)_{T,P,\bar{N}_{s'\neq s}}, \tag{15.10}$$

where all these derivatives are taken at constant $\bar{N}_{s'}$, where $s' = 1, \dots, s-1, s+1, \dots, m$.

15.1.1. *Gibbs Free Energy vs.* $\mu_s$

Similarly to the case of one species, there is a special relationship between the chemical potentials and Gibbs free energy (cf. §14.6.2). Indeed, since $G = U - TS + PV$ is extensive and so are all the particle numbers $\bar{N}_1, \dots, \bar{N}_m$, scaling the system by $\lambda$ gives

$$G(P, T, \lambda\bar{N}_1, \dots, \lambda\bar{N}_m) = \lambda G(P, T, \bar{N}_1, \dots, \bar{N}_m), \tag{15.11}$$

which, upon differentiation with respect to $\lambda$ and then setting $\lambda = 1$, gives us [cf. (14.69)]

$$\sum_s \underbrace{\left(\frac{\partial G}{\partial \bar{N}_s}\right)_{T,P,\bar{N}_{s'\neq s}}}_{\substack{=\,\mu_s,\\ \text{see (15.10)}}} \bar{N}_s = G, \tag{15.12}$$

whence it follows that the Gibbs free energy of a multispecies system is "the total amount of chemical potential" amongst all species:

$$\boxed{G = \sum_s \mu_s \bar{N}_s}\,. \tag{15.13}$$

Note that this implies, via (15.5), that

$$\Phi = U - TS - G = -PV, \tag{15.14}$$

and the equation of state can again be obtained from this, as in (14.74).

15.1.2. *Fractional Concentrations*

Since $\mu_s$ are all intensive [this follows from (15.10)], they do not depend on the total number of particles, but only on other intensive quantities, viz., pressure, temperature and the *fractional concentrations* of all the species:

$$\mu_s = \mu_s(P, T, c_1, \dots, c_{m-1}), \tag{15.15}$$

where

$$c_s = \frac{\bar{N}_s}{\bar{N}}, \quad \bar{N} = \sum_s \bar{N}_s. \tag{15.16}$$

There are only $m-1$ independent fractional concentrations as, obviously, $\sum_s c_s = 1$.

### 15.2. *Particle Equilibrium and Gibbs Phase Rule*

Arguing exactly like we did in §14.3, one can prove that *across a system in equilibrium,* $\mu_s = \text{const}$ *for each species* (**exercise**). Note that chemical potentials of *different* species do *not* need to be equal even if they are in contact within a system.

There is a useful immediate consequence of this. Consider a system of $m$ species, each of which can be in $r$ phases. Then, in equilibrium,

$$\begin{aligned} &\mu_1^{(\text{phase }1)} = \mu_1^{(\text{phase }2)} = \dots = \mu_1^{(\text{phase }r)}, \\ &\dots \\ &\mu_m^{(\text{phase }1)} = \mu_m^{(\text{phase }2)} = \dots = \mu_m^{(\text{phase }r)}, \end{aligned} \tag{15.17}$$

where each $\mu_s^{(\text{phase }p)}$ is a function of $P$, $T$ and the fractional concentrations of all species in phase $p$:

$$\mu_s^{(\text{phase }p)} = \mu_s^{(\text{phase }p)}\left(P, T, c_1^{(\text{phase }p)}, \dots, c_{m-1}^{(\text{phase }p)}\right). \tag{15.18}$$

Thus, we have $m(r-1)$ equations for $2 + r(m-1)$ unknowns. In order for this system of equations to have a solution (not necessarily unique), the number of equations must not exceed the number of unknowns, viz.,

$$\boxed{r \leqslant m + 2}\,. \tag{15.19}$$

This is called the *Gibbs phase rule*. It implies, for example, that a single species ($m = 1$) can only support an equilibrium state with $r \leqslant 3$ coexisting phases (e.g., gas, liquid, solid).

The set of equations (15.17) is the starting point for the *theory of phase transitions*, of which more will be said in Part VII.

*NB:* There was a subtlety in (15.18): we assumed that the chemical potential of each phase depended on fractional concentrations of *all* species but *only in that phase*. That means that each phase is internally homogeneous and has a well-defined thermodynamic state, which would be the case if, e.g., phases were spatially localised and interacting only via interfacial surfaces (think of ice in water). We are still allowing different species to be mixed up within the same phase (e.g., a solution of different fluids or mixture of gases). There is no problem if some species in some phases are immiscible (this can easily happen with solids): for those species in those phases, the chemical potential will simply not depend on the concentrations at all (since there can be only one and it is, therefore, 100%), but that does not contradict the formal statement (15.18) and so does not upset the variable count. You might worry that this leaves the overall number of particles $\bar{N}^{(\text{phase }p)} = \sum_s \bar{N}_s^{(\text{phase }p)}$ in each phase undetermined because $c_s^{(\text{phase }p)} = \bar{N}_s^{(\text{phase }p)}/\bar{N}^{(\text{phase }p)}$ only tells us what fraction of $\bar{N}^{(\text{phase }p)}$ is taken up by species $s$. But if the total (mean) number of particles $\bar{N}_s$ of each species in the system is fixed and known, then we have $m$ additional equations

$$\sum_p c_s^{(\text{phase } p)} \bar{N}^{(\text{phase } p)} = \bar{N}_s \tag{15.20}$$

for $r$ additional unknowns $\bar{N}^{(\text{phase } p)}$. This brings our equation count to $m(r-1)+m = mr$ and our unknown count to $2+r(m-1)+r = 2+mr$. Thus, at each given $T$, $P$, and a full set of $\bar{N}_s$ (the latter being extensive variables), we have a unique equilibrium.

### 15.3. *Chemical Equilibrium*

Now let us work out how $\mu_s$ for *different* species are related to each other in equilibrium. Obviously, they need to be related at all only if these different species can transmutate into each other and so the system can adjust their fractional concentrations in its quest for an optimal (maximum-entropy) equilibrium state—i.e., if these species are subject to *chemical (or atomic, or particle) reactions.* These reactions can usually be expressed in the form

$$\sum_s \nu_s A_s = 0, \tag{15.21}$$

where $A_s$ designate the species and $\nu_s$ are integers encoding their relative amounts participating in a reaction. For example,

$$2H_2 + O_2 = 2H_2O \tag{15.22}$$

is encoded by $A_1 = H_2$, $A_2 = O_2$, $A_3 = H_2O$ and $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = -2$;

$$e^+ + e^- = 2\gamma \quad \Leftrightarrow \quad \nu_1 = 1, \nu_2 = 1, \nu_3 = -2 \tag{15.23}$$

(pair production/annihilation),

$$p^+ + e^- = \text{H} \quad \Leftrightarrow \quad \nu_1 = 1, \nu_2 = 1, \nu_3 = -1 \tag{15.24}$$

(ionisation/recombination of atomic hydrogen), etc. The set of numbers $\{\nu_s\}$ fully specifies a reaction, as far as Statistical Mechanics is concerned (as we are about to see). In general, *reactions can go both ways*, until there is a stable soup where the fractional concentration of each species has assumed its equilibrium value.

How do we find these equilibrium values?

At constant $T$ and $P$ (which is the usual set up in a chemistry lab), in order to find the equilibrium, one must minimise Gibbs free energy, viz., from (15.9),

$$\mathrm{d}G = \sum_s \mu_s \mathrm{d}\bar{N}_s = 0. \tag{15.25}$$

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The proof of this is the standard so-called "availability" argument, which is as follows. Consider a system in contact with environment. As it equilibrates, the total energy is conserved,

$$\mathrm{d}(U + U_{\text{env}}) = 0, \tag{15.26}$$

whereas the total entropy must grow,

$$\mathrm{d}(S + S_{\text{env}}) \geqslant 0. \tag{15.27}$$

From (15.26),

$$\mathrm{d}U = -\mathrm{d}U_{\text{env}} = -T_{\text{env}}\mathrm{d}S_{\text{env}} + P_{\text{env}}\mathrm{d}V_{\text{env}}. \tag{15.28}$$

Note that the number of particles in the environment does not change: we assume that all the exchanges/transmutations of matter occur within the system. Since $\mathrm{d}V_{\text{env}} = -\mathrm{d}V$ (the volume of the world is constant), this gives

$$T_{\text{env}}\mathrm{d}S_{\text{env}} = -\mathrm{d}U - P_{\text{env}}\mathrm{d}V. \tag{15.29}$$

Now, from this and (15.27),

$$0 \leqslant T_{\rm env}({\rm d}S + {\rm d}S_{\rm env}) = T_{\rm env}{\rm d}S - {\rm d}U - P_{\rm env}{\rm d}V = -{\rm d}(U - T_{\rm env}S + P_{\rm env}V) = -{\rm d}G. \quad (15.30)$$

Thus, $\mathrm{d}G \leqslant 0$, so the final equilibrium is achieved at the minimum value of $G$. The same argument mandates $\mathrm{d}F \leqslant 0$ when $V = \text{const}$ and, unsurprisingly, $\mathrm{d}S \geqslant 0$ when also $U = \text{const}$, i.e., when the system is isolated.

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**Exercise 15.1.** In what circumstances is the equilibrium achieved at minimum energy (i.e., $\mathrm{d}U \leqslant 0$)? This is called classical mechanics!

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The formula (15.21) for the chemical reaction implies that, as the reaction occurs,

$$\mathrm{d}\bar{N}_1 : \mathrm{d}\bar{N}_2 : \cdots : \mathrm{d}\bar{N}_m = \nu_1 : \nu_2 : \cdots : \nu_m. \quad (15.31)$$

Therefore, (15.25) becomes

$$\boxed{\sum_s \nu_s \mu_s = 0}\,. \quad (15.32)$$

This is the *equation of chemical equilibrium*. There will be an equation like this for each reaction that the system is capable of (each specified by a set of numbers $\{\nu_s\}$). All these equations together give a set of constraints on fractional concentrations $c_1, \dots, c_{m-1}$ because these are the only variables that $\mu_s$ depends on, at constant $P$ and $T$ [see (15.15)]. Note that the number of equations (15.32) is not necessarily equal to the number of unknowns, so solutions do not necessarily exist or are unique.

### 15.4. *Chemical Equilibrium in a Mixture of Classical Ideal Gases: Law of Mass Action*

In order to apply (15.32), we need explicit expressions for $\mu_s(P, T, c_1, \dots, c_{m-1})$. We can get them from, e.g., (15.4), which we can rewrite so:

$$c_s = \frac{k_{\rm B}T}{\bar{N}} \frac{\partial \ln \mathcal{Z}}{\partial \mu_s} \quad (15.33)$$

(a system of $m$ equations for $s = 1, \dots, m$). This means that we need to know the grand partition function for our mixture. If the mixture is of classical ideal gases, we can calculate it by direct generalisation of the relevant results of §14.4. Since the gases are ideal, there are no interactions between particles and so each species within a gas behaves as a separate subsystem,[64] in equilibrium with the rest. Therefore,

$$\mathcal{Z} = \prod_s \mathcal{Z}_s = \exp\left(\sum_s Z_{1s} e^{\beta\mu_s}\right), \quad (15.34)$$

where $\mathcal{Z}_s$ is the grand partition function of the species $s$, we have used (14.40), and

$$Z_{1s} = \frac{V}{\lambda_{\rm th\mathit{s}}^3} Z_{1s}^{(\rm internal)}, \quad \lambda_{\rm th\mathit{s}} = \hbar\sqrt{\frac{2\pi}{m_s k_{\rm B} T}}, \quad (15.35)$$

is the single-particle partition function of species $s$.

---

**Exercise 15.2.** Derive (15.34) directly, by constructing the microstates of a mixture of ideal gases and then summing over all these microstates to get $\mathcal{Z}$.

---

[64] This is not true in general for multicomponent chemical systems, as they can, in principle, interpenetrate, be strongly interacting and have collective energy levels not simply equal to sums of the energy levels of individual components.

Using (15.34) in (15.33), we find

$$c_s\bar{N} = k_{\rm B}T\frac{\partial}{\partial\mu_s}\sum_{s'} Z_{1s'}e^{\beta\mu_{s'}} = Z_{1s}e^{\beta\mu_s}, \tag{15.36}$$

and, after using (15.35), we get [cf. (14.43) and (14.46)],

$$\mu_s = -k_{\rm B}T\ln\frac{Z_{1s}}{c_s\bar{N}} = k_{\rm B}T\ln\left(\frac{c_s n\lambda_{\rm th\mathit{s}}^3}{Z_{1s}^{(\rm internal)}}\right) = k_{\rm B}T\ln\left(\frac{c_s}{Z_{1s}^{(\rm internal)}}\frac{P\lambda_{\rm th\mathit{s}}^3}{k_{\rm B}T}\right), \tag{15.37}$$

where $n = \bar{N}/V$ is the overall number density of the mixture and we have used *Dalton's law:* total pressure is the sum of the pressures of individual species,

$$P = \sum_s n_s k_{\rm B}T = nk_{\rm B}T \tag{15.38}$$

[see Exercise 4.3b or convince yourself, starting from (15.14), that this is true].
Finally, inserting (15.37) into (15.32), we find

$$k_{\rm B}T\sum_s \nu_s\ln\left(\frac{c_s}{Z_{1s}^{(\rm internal)}}\frac{P\lambda_{\rm th\mathit{s}}^3}{k_{\rm B}T}\right) = 0. \tag{15.39}$$

Thus, the fractional concentrations must obey

$$\sum_s \nu_s\ln c_s = -\sum_s \nu_s\ln\left(\frac{P\lambda_{\rm th\mathit{s}}^3}{Z_{1s}^{(\rm internal)}k_{\rm B}T}\right), \tag{15.40}$$

or, to write this in a commonly used form highlighting pressure and temperature dependence,

$$\boxed{\prod_s c_s^{\nu_s} = P^{-\sum_s\nu_s}\underbrace{\prod_s\left(\frac{k_{\rm B}T}{\lambda_{\rm th\mathit{s}}^3}Z_{1s}^{(\rm internal)}\right)^{\nu_s}}_{\text{function of } T \text{ only}} \equiv K(P,T)}\,. \tag{15.41}$$

The right-hand side of this equation is called the *chemical equilibrium constant*, which, for any given reaction (defined by $\nu_s$'s), is a known function of $P$, $T$, and the microphysics of the participating particles. The equation itself is known as the *Law of Mass Action* (because of the particle masses $m_s$ entering $K(P,T)$ via $\lambda_{\rm th\mathit{s}}$).

Together with the requirement that $\sum_s c_s = 1$, (15.41) constrains fractional concentrations in chemical equilibrium. It also allows one to determine in which direction the reaction will go from some initial non-equilibrium state:

—if $\prod_s c_s^{\nu_s} > K(P,T)$, the reaction is *direct*, i.e., the concentrations $c_s$ of the species with $\nu_s > 0$, which are on the left-hand side of (15.21), will go down, while those of the species with $\nu_s < 0$, on the right-hand side of (15.21), will go up;

—if $\prod_s c_s^{\nu_s} < K(P,T)$, the reaction is *reverse*.

This is all the chemistry you need to know! (At least in this course.)

**Exercise 15.3. Partially Ionised Plasma.** Consider atomic-hydrogen gas at a high enough temperature that ionisation and recombination are occurring. The reaction is given by (15.24). Our goal is to find, as a function of density and temperature (or pressure and temperature), the degree of ionisation $\chi = n_p/n$, where $n_p$ is the proton number density, $n = n_{\rm H} + n_p$ is the total number density of hydrogen, ionised or not, and $n_{\rm H}$ is the number density of the un-ionised H atoms. Note that $n$ is fixed (conservation of nucleons). Assume overall charge neutrality of the system.

(a) What is the relation between chemical potentials of the H, $p$ and $e$ gases if the system is in chemical equilibrium?

(b) Treating all three species as classical ideal gases, show that in equilibrium,

$$\boxed{\frac{n_e n_p}{n_{\rm H}} = \left(\frac{m_e k_{\rm B} T}{2\pi\hbar^2}\right)^{3/2} e^{-R/k_{\rm B}T}}, \tag{15.42}$$

where $R = 13.6$ eV (1 Rydberg) is the ionisation energy of hydrogen. This formula is known as the *Saha equation*. *Hint.* Remember that you have to include the internal energy levels into the partition function for the hydrogen atom. You may assume that only the ground state energy level $-R$ matters (i.e., neglect all excited states).

(c) Find the degree of ionisation $\chi = n_p/n$ as a function of $n$ and $T$. Does $\chi$ go up or down as density is decreased? Why? Consider a cloud of hydrogen with $n \sim 1$ cm$^{-3}$. Roughly at what temperature would most of it be ionised? These are approximately the conditions in the so called "warm" phase of the interstellar medium—the stuff that much of the Galaxy is filled with (although, admittedly, the Law of Mass Action is not thought to be a very good approximation for interstellar medium, because it is not exactly in equilibrium).

(d) Now find an expression for $\chi$ as a function of total gas pressure $P$ and temperature $T$. Sketch $\chi$ as a function of $T$ at several constant values of $P$.

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# PART VI
# Quantum Gases

## 16. Quantum Ideal Gases

So far, in all our calculations of partition functions for gases, we have stayed within the classical limit, where the key assumption was that the number of single-particle states available to particles was much greater than the number of these particles, so the probability of any one particle occupying any given single-particle state was small and, therefore, the probability of more than one particle laying claim to the same state could be completely discounted. The time has now come to relax this assumption, but first, let me explain what are those *quantum correlations* dealing with which I have so far been so determined to avoid.

### 16.1. *Fermions and Bosons*

• Consider a 2-particle wave function, $\psi(1,2)$, where the first argument corresponds to the first particle, the second to the second and the notation means that the first is in state 1 and the second in state 2.

• Now swap the two particles: $\psi(1,2) \to \psi(2,1)$.

• If the particles are indistinguishable, this operation cannot change any observables, so the probability density cannot change under the swapping operation:

$$|\psi(2,1)|^2 = |\psi(1,2)|^2 \quad \Rightarrow \quad \psi(2,1) = e^{i\phi}\psi(1,2) \tag{16.1}$$

(swapping can only bring in a phase factor).

• Apply the swapping operation twice:

$$\psi(2,1) = e^{i\phi}\psi(1,2) = e^{2i\phi}\psi(2,1) \quad \Rightarrow \quad e^{2i\phi} = 1 \quad \Rightarrow \quad e^{i\phi} = \pm 1. \tag{16.2}$$

This argument tells us that there can be (and, as it turns out, there are) two types of particles, corresponding to two possible *exchange symmetries:*[65]

$$1) \quad \boxed{\psi(2,1) = \psi(1,2)}\,, \tag{16.3}$$

called *bosons*—they can be proven to be particles with *integer spin*, e.g., photons (spin 1), $^4$He atoms (spin 0);

$$2) \quad \boxed{\psi(2,1) = -\psi(1,2)}\,, \tag{16.4}$$

called *fermions*—these are particles with *half-integer spin*, e.g., $e$, $n$, $p$, $^3$He (spin 1/2).

The fermions are subject to the *Pauli exclusion principle:* if the states 1 and 2 are the same, then

$$\psi(1,1) = -\psi(1,1) = 0, \tag{16.5}$$

so *no two fermions can be in the same state.* This is precisely an example of *quantum correlations*: even though the gas is ideal and so the fermions are non-interacting, the system as a whole "knows" which single-particle states are occupied and so are unavailable to other particles.

What does all this mean for the statistical mechanics of systems composed of bosons or fermions? Recall that the microstates of a box of ideal gas were specified in terms of occupation numbers $n_i$ of single-particle states $i$.[66] What we have just inferred from the exchange symmetries determines what values these occupation numbers can take:

—for bosons, $n_i = 0, 1, 2, 3, \dots$ (any integer),

—for fermions, $n_i = 0$ or 1 (no more than 1 particle in each state).

Armed with this knowledge, we are ready to start computing.

### 16.2. *Partition Function*

The grand partition function is given by (14.9), where the microstates are $\alpha = \{n_i\}$ (sets of occupation numbers), the energy levels of the system are

$$E_\alpha = \sum_i n_i \varepsilon_i \tag{16.6}$$

($\varepsilon_i$ are the energies of the single-particle states $i$), and the particle number in state $\alpha$ is

$$N_\alpha = \sum_i n_i. \tag{16.7}$$

Then

$$\begin{aligned}\mathcal{Z} &= \sum_\alpha e^{-\beta(E_\alpha - \mu N_\alpha)} = \sum_{\{n_i\}} e^{-\beta\sum_i n_i(\varepsilon_i - \mu)} \\ &= \underbrace{\sum_{n_1}\sum_{n_2}\sum_{n_3}\dots}_{\substack{\text{over all possible} \\ \text{values of } \{n_i\}}} \prod_i e^{-\beta n_i(\varepsilon_i - \mu)} = \prod_i \sum_{n_i} e^{-\beta n_i(\varepsilon_i - \mu)}.\end{aligned} \tag{16.8}$$

---

[65] See Landau & Lifshitz (1981), §61–62 for a rigorous generalisation of this argument to $N$-particle wave functions and the derivation of the connection between a particle's spin and the exchange symmetry.

[66] In §11, $i$ was $\boldsymbol{k}$, but in general, single-particle states will depend on other quantum numbers as well, e.g., spin, angular momentum, vibrational levels, etc.—but they are still discrete, so I shall continue indexing them by $i$.

For fermions, $n_i = 0$ or 1, so the sum $\sum_{n_i}$ has only two members and so

$$\mathcal{Z} = \prod_i \left[1 + e^{-\beta(\varepsilon_i - \mu)}\right]. \tag{16.9}$$

For bosons, $n_i = 0, 1, 2, 3, \dots$, so

$$\mathcal{Z} = \prod_i \underbrace{\sum_{n_i=0}^{\infty} \left[e^{-\beta(\varepsilon_i - \mu)}\right]^{n_i}}_{\text{geometric series}} = \prod_i \frac{1}{1 - e^{-\beta(\varepsilon_i - \mu)}}. \tag{16.10}$$

Or, to write this compactly,

$$\boxed{\ln \mathcal{Z} = \pm \sum_i \ln \left[1 \pm e^{-\beta(\varepsilon_i - \mu)}\right]}, \tag{16.11}$$

where "+" corresponds to fermions and "−" to bosons.

### 16.3. *Occupation Number Statistics and Thermodynamics*

The probability for a given set of occupation numbers to occur is given by the grand canonical distribution (14.8):

$$p_\alpha \equiv p(n_1, n_2, n_3, \dots) = \frac{1}{\mathcal{Z}} e^{-\beta \sum_i n_i (\varepsilon_i - \mu)}. \tag{16.12}$$

Therefore, the *mean occupation number* of a single-particle state $j$ is

$$\bar{n}_j \equiv \langle n_j \rangle = \sum_{\{n_i\}} n_j\, p(n_1, n_2, n_3, \dots) = \frac{1}{\mathcal{Z}} \sum_{\{n_i\}} n_j\, e^{-\beta \sum_i n_i (\varepsilon_i - \mu)} = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_j}. \tag{16.13}$$

Using (16.11), we get

$$\boxed{\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} \pm 1}}. \tag{16.14}$$

Thus, we can predict how many particles will be in any given state on average (this is exactly the same as calculating the *distribution function*, which was our main vehicle in Kinetic Theory; see §11.11). The "+" sign in (16.14) gives us the *Fermi–Dirac statistics* and the "−" sign the *Bose–Einstein statistics*.

---

**Exercise 16.1. Entropy of Fermi and Bose Gases out of Equilibrium.** It is possible to construct the statistical mechanics of quantum ideal gases directly in terms of occupation numbers. In the spirit of Gibbs (§12.1.3), consider an ensemble of $\mathcal{N}$ copies of our system (gas in a box). Let $\mathcal{N}_i$ be the number of particles that are in the single-particle state $i$ across this entire über-system. Then the average occupation number of the state $i$ per copy is $\bar{n}_i = \mathcal{N}_i/\mathcal{N}$. If the number of ways in which a given assignment $\{\mathcal{N}_1, \mathcal{N}_2, \dots, \mathcal{N}_i, \dots\}$ of particles to single-particle states can be achieved is $\Omega_{\mathcal{N}}(\mathcal{N}_1, \mathcal{N}_2, \dots)$, then the Gibbs entropy associated with the set of occupation numbers $(\bar{n}_1, \bar{n}_2, \dots, \bar{n}_i, \dots)$ will be

$$S_{\mathrm{G}}(\bar{n}_1, \bar{n}_2, \dots) = \frac{\ln \Omega_{\mathcal{N}}(\mathcal{N}_1, \mathcal{N}_2, \dots)}{\mathcal{N}} \tag{16.15}$$

in the limit $\mathcal{N} \to \infty$ and all $\mathcal{N}_i \to \infty$ while keeping $\bar{n}_i$ constant. This is very similar to the construction in §§8.1.3 or 12.1.3 of the Gibbs entropy of a set of probabilities of microstates, except we now have different rules about how many particles can be in any given microstate $i$:

— for fermions, each copy of the system in the ensemble can have only one or none of the $\mathcal{N}_i$ particles available for each state $i$;

— for bosons, the $\mathcal{N}_i$ particles in each state $i$ can be distributed completely arbitrarily between the $\mathcal{N}$ copies.

(a) Prove that the Gibbs entropy, as defined above, is

$$S_{\rm G} = -\sum_i \left[\bar{n}_i \ln \bar{n}_i \pm (1 \mp \bar{n}_i) \ln(1 \mp \bar{n}_i)\right], \tag{16.16}$$

where the upper sign is for fermions and the lower for bosons. *Hint.* Observe that $\Omega_{\mathcal{N}}(\mathcal{N}_1, \mathcal{N}_2, \dots) = \prod_i \Omega_i$, where $\Omega_i$ is the number of ways to assign the $\mathcal{N}_i$ particles available for the microstate $i$ to the $\mathcal{N}$ copies in the ensemble.

Note that (16.16) certainly holds for Fermi and Bose gases *in equilibrium*, i.e., if the occupation numbers $\bar{n}_i$ are given by (16.14) (convince yourself that this is the case), but you have shown now that it also holds *out of equilibrium*, i.e., for arbitrary sets of occupation numbers (arbitrary *particle distributions*).

(b) Considering a system with fixed mean energy and number of particles and maximising $S_{\rm G}$, derive from (16.16) the Fermi–Dirac and Bose–Einstein formulae (16.14) for the mean occupation numbers in equilibrium.

(c) Devise a way to treat a classical ideal gas by the same method.

---

The machinery you have learned from Exercise 16.1 can be used in a somewhat unexpected way to think of the statistics of self-gravitating systems (e.g., distribution of energies of stars in a galaxy) or of collisionless plasmas (cf. Exercise 6.3)—generally, systems of many particles interacting via some field (gravitational, electromagnetic) but not experiencing particle-on-particle collisions. It turns out that one can argue that, subject to certain assumptions, these (classical!) systems strive towards a variant of the Fermi–Dirac distribution known as the *Lynden-Bell distribution* (after the seminal paper by Lynden-Bell 1967). If you are intrigued by this, read §10 of Schekochihin (2025).

---

The formula (16.14) is useful provided we know

—the single-particle energy levels $\varepsilon_i$ for a given system (which we get from Quantum Mechanics),

—the chemical potential $\mu(n, T)$ ($n = N/V$ is the overall particle density), the equation for which is simply

$$\boxed{N = \sum_i \bar{n}_i} \tag{16.17}$$

[equivalent to (14.13)]. From this point on, I will drop the bars on $N$ as we really are interested in the case with a fixed number of particles again and the use of grand canonical ensemble was a matter of analytical convenience. As I explained at the end of §14.1 and around (14.25), canonical results are recoverable from the grand canonical ones because they correspond to the special case of $N_\alpha = N$ for all $\alpha$ (with $N$ treated as a parameter, akin to $V$).

---

**Exercise 16.2.** Show that using (16.11) in (14.13) gives the same result as using (16.14) in (16.17).

---

To construct the thermodynamics of a quantum gas, we then need to calculate the mean energy

$$\boxed{U = \sum_i \varepsilon_i \bar{n}_i} \tag{16.18}$$

[equivalent to (14.11)], the grand potential (14.26) and the equation of state (14.74),

$$\boxed{\Phi = -k_{\rm B}T\ln\mathcal{Z} \quad\Rightarrow\quad P = -\frac{\Phi}{V}}, \tag{16.19}$$

and the entropy

$$\boxed{S = \frac{U - \Phi - \mu N}{T}} \tag{16.20}$$

[equivalent to (14.28)], whence we can get the heat capacities, etc.

## 16.4. *Calculations in Continuum Limit*

[Literature: Landau & Lifshitz (1980), §56; Schrödinger (1990), Ch. VIII]

Let us now implement the programme outlined at the end of §16.3.

### 16.4.1. *From Sums to Integrals*

We shall have to learn how to calculate various discrete sums over single-particle states. For this, we convert them to continuous integrals in the following way.

The single-particle states are

$$i = (\boldsymbol{p}, s_z), \tag{16.21}$$

where $\boldsymbol{p} = \hbar\boldsymbol{k}$ is the particle's momentum (with the wave number $\boldsymbol{k}$ quantised according to (11.3) if the gas is assumed to sit in a box of volume $V = L_xL_yL_z$) and $s_z = -s, \dots, s$ is the projection of the particle's spin on an arbitrary axis, allowed $2s+1$ possible values, with $s$ an integer or a half-integer number.

For a non-relativistic gas ($k_{\rm B}T \ll mc^2$), the energy of the state $i$ is

$$\varepsilon_i = \varepsilon(k) = \frac{\hbar^2k^2}{2m}, \tag{16.22}$$

independent of the spin or of the direction of $\boldsymbol{k}$.

---

More generally,

$$\varepsilon(k) = \sqrt{m^2c^4 + \hbar^2k^2c^2}. \tag{16.23}$$

For ultrarelativistic particles ($\hbar kc \gg mc^2$),

$$\varepsilon(k) \approx \hbar kc. \tag{16.24}$$

An example of the latter are photons (§19; see also Exercise 16.6).

---

Since $\bar{n}_i$ only depends on $k = |\boldsymbol{k}|$, via $\varepsilon(k)$, we can approximate the sum over single-particle states with an integral as follows, using the same trick as in (11.7),

$$\sum_i = (2s+1)\sum_{\boldsymbol{k}} = \frac{(2s+1)V}{(2\pi)^3}\int {\rm d}^3\boldsymbol{k} = \frac{(2s+1)V}{(2\pi)^3}\int_0^\infty 4\pi k^2{\rm d}k$$
$$= \frac{(2s+1)V}{2\pi^2}\int_0^\infty {\rm d}k\, k^2 \equiv \int {\rm d}k\, g(k), \tag{16.25}$$

where the *density of states* is

$$g(k) = \frac{(2s+1)V}{2\pi^2}k^2 \tag{16.26}$$

(this was already introduced and discussed in §11.4, except for the spin factor: until now, we have tacitly assumed spinless particles—if they do in fact have spin, this is equivalent to setting $Z_1^{(\text{internal})} = 2s+1$).

In fact, since the occupation numbers always depend on $k$ via $\varepsilon$, $\bar{n}_i = \bar{n}(\varepsilon)$, it is convenient to change the integration variable from $k$ to $\varepsilon$: as

$$k = \frac{\sqrt{2m\varepsilon}}{\hbar} \quad \text{and} \quad \mathrm{d}k = \frac{1}{\hbar}\sqrt{\frac{m}{2\varepsilon}}\,\mathrm{d}\varepsilon, \tag{16.27}$$

we have

$$g(k)\mathrm{d}k = \frac{(2s+1)V}{2\pi^2}\frac{2m\varepsilon}{\hbar^2}\frac{1}{\hbar}\sqrt{\frac{m}{2\varepsilon}}\,\mathrm{d}\varepsilon \equiv g(\varepsilon)\mathrm{d}\varepsilon, \tag{16.28}$$

where the density of states per unit energy is

$$\boxed{g(\varepsilon) = \frac{(2s+1)Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\sqrt{\varepsilon} = \frac{2(2s+1)}{\sqrt{\pi}}\frac{V}{\lambda_{\text{th}}^3}\sqrt{\varepsilon}\,\beta^{3/2}}\,. \tag{16.29}$$

From (16.25),

$$\boxed{\sum_i = \int_0^\infty \mathrm{d}\varepsilon\, g(\varepsilon)}\,. \tag{16.30}$$

16.4.2. *Chemical Potential of a Quantum Ideal Gas*

We are now ready to compute the sum (16.17) for the occupation numbers given by (16.14)

$$\begin{aligned} N = \sum_i \bar{n}_i &= \int_0^\infty \frac{\mathrm{d}\varepsilon\, g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}\pm 1} = \frac{2(2s+1)}{\sqrt{\pi}}\frac{V}{\lambda_{\text{th}}^3}\int_0^\infty \frac{\mathrm{d}\varepsilon\sqrt{\varepsilon}\,\beta^{3/2}}{e^{\beta(\varepsilon-\mu)}\pm 1} \\ &= \frac{2(2s+1)}{\sqrt{\pi}}\frac{V}{\lambda_{\text{th}}^3}\int_0^\infty \frac{\mathrm{d}x\sqrt{x}}{e^{x-\beta\mu}\pm 1}, \end{aligned} \tag{16.31}$$

where I have changed the integration variable to $x = \beta\varepsilon$.

As I already explained in §16.3, this is an implicit equation for $\mu(n,T)$: making the density ($n = N/V$) dependence explicit,

$$\boxed{\frac{n}{n_{\text{Q}}} \equiv \frac{n\lambda_{\text{th}}^3}{2s+1} = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\mathrm{d}x\sqrt{x}}{e^{x-\beta\mu}\pm 1}} \quad \Rightarrow \quad \mu = \mu(n,T), \tag{16.32}$$

where $n_{\text{Q}} = (2s+1)/\lambda_{\text{th}}^3$ is the "quantum concentration" [recall (11.31)].

16.4.3. *Classical Limit*

Before we move on, let us reassure ourselves that we are doing the right thing by showing that we can recover previously known classical results in the classical limit (at high temperatures and low densities). Equation (16.32) has the form

$$\frac{n\lambda_{\text{th}}^3}{2s+1} = f(\beta\mu). \tag{16.33}$$

For a hot dilute gas ($n \to 0$ and/or $T \to \infty$), the left-hand side tends to zero and, therefore, the function $f(\beta\mu)$ must do the same. It is not hard to see that $f(\beta\mu) \to 0$ if

$e^{-\beta\mu} \to \infty$:

$$f(\beta\mu) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx\sqrt{x}}{e^{x-\beta\mu} \pm 1} \approx \frac{2}{\sqrt{\pi}}\, e^{\beta\mu} \underbrace{\int_0^\infty dx\sqrt{x}\, e^{-x}}_{=\sqrt{\pi}/2} = e^{\beta\mu} \to 0. \tag{16.34}$$

Then, from (16.33), in the classical limit,

$$\frac{n\lambda_{\rm th}^3}{2s+1} \approx e^{\beta\mu} \quad \Rightarrow \quad \boxed{\mu \approx k_{\rm B}T \ln\left(\frac{n\lambda_{\rm th}^3}{2s+1}\right)}, \tag{16.35}$$

which is precisely the classical expression (14.46) with $Z_1^{(\rm internal)} = 2s+1$, q.e.d.!

Note that we have also confirmed that the classical limit is achieved when

$$\boxed{\frac{n}{n_{\rm Q}} = \frac{n\lambda_{\rm th}^3}{2s+1} \ll 1}, \tag{16.36}$$

as anticipated in our derivation of the partition function for the classical ideal gas [see (11.30)].

---

Let us be thorough and confirm that we can recover our familiar expression for the grand and ordinary partition functions of an ideal gas in the classical limit. As we now know, we must take $e^{\beta\mu} \ll 1$. From (16.11), we get in this limit

$$\ln \mathcal{Z} \approx \sum_i e^{\beta\mu} e^{-\beta\varepsilon_i} = e^{\beta\mu} Z_1 \quad \Rightarrow \quad \mathcal{Z} \approx e^{Z_1 e^{\beta\mu}}, \tag{16.37}$$

which is (14.40), the classical grand partition function. Note that, in the classical limit, using (16.35),

$$Z_1 = \frac{V}{\lambda_{\rm th}^3}(2s+1) = Ne^{-\beta\mu} \quad \Rightarrow \quad \mathcal{Z} = e^N. \tag{16.38}$$

Furthermore, if $N$ is fixed, we find from (14.16) that the ordinary partition function is

$$Z = \frac{\mathcal{Z}}{(e^{\beta\mu})^N} \approx \underbrace{\left(\frac{2s+1}{n\lambda_{\rm th}^3}\right)}_{=\frac{Z_1}{N}}{}^{N} e^N = \frac{Z_1^N}{N^N e^{-N}} \approx \frac{Z_1^N}{N!}, \tag{16.39}$$

as we indeed surmised for the classical ideal gas in §11.9 by neglecting quantum correlations [see (11.26)].

---

Finally, as anticipated in §11.11, we can also recover Maxwell's distribution from the occupation-number statistics in the classical limit: from (16.14) and using (16.35),

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1} \approx e^{\beta\mu} e^{-\beta\varepsilon_i} = \frac{n\lambda_{\rm th}^3}{2s+1}\, e^{-\beta\varepsilon_i}. \tag{16.40}$$

This is exactly the expression (11.43) that we expected for the occupation numbers in a classical ideal gas, so as to recover the Maxwellian distribution. Note that (16.40) makes it obvious that in the classical limit, $\bar{n}_i \ll 1$, i.e., all microstates are mostly unoccupied—just as we argued (in §11.9) must be the case in order for quantum correlations to be negligible.

Obviously, none of this is a great surprise, but it is nice how neatly it all works out.

16.4.4. *Mean Energy of a Quantum Ideal Gas*

In a similar vein to §16.4.2, from (16.18),

$$U = \sum_i \bar{n}_i \varepsilon_i = \int_0^\infty \frac{\mathrm{d}\varepsilon\, g(\varepsilon)\, \varepsilon}{e^{\beta(\varepsilon-\mu)} \pm 1} = \frac{2(2s+1)}{\sqrt{\pi}} \frac{V}{\lambda_{\rm th}^3} k_{\rm B}T \int_0^\infty \frac{\mathrm{d}\varepsilon\, \varepsilon^{3/2} \beta^{5/2}}{e^{\beta(\varepsilon-\mu)} \pm 1}$$

$$\Rightarrow \boxed{U = N k_{\rm B} T \left(\frac{n_{\rm Q}}{n} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\mathrm{d}x\, x^{3/2}}{e^{x-\beta\mu} \pm 1}\right)}. \tag{16.41}$$

**Exercise 16.3.** Via a calculation analogous to what was done in §16.4.3, check that the expression in the brackets in (16.41) is equal to 3/2 in the classical limit [as it ought to be: see (11.34)].

16.4.5. *Grand Potential of a Quantum Ideal Gas*

From (16.19) and (16.11),

$$\Phi = -k_{\rm B}T \ln \mathcal{Z} = \mp k_{\rm B}T \sum_i \ln\left[1 \pm e^{-\beta(\varepsilon_i - \mu)}\right] = \mp k_{\rm B}T \int_0^\infty \mathrm{d}\varepsilon\, g(\varepsilon) \ln\left[1 \pm e^{-\beta(\varepsilon-\mu)}\right]$$

$$= \mp N k_{\rm B}T \frac{n_{\rm Q}}{n} \frac{2}{\sqrt{\pi}} \underbrace{\int_0^\infty \mathrm{d}x \sqrt{x}\, \ln\left(1 \pm e^{-x+\beta\mu}\right)}_{\begin{array}{c} = \int_0^\infty \mathrm{d}x \left(\frac{2}{3}\frac{\mathrm{d}}{\mathrm{d}x} x^{3/2}\right) \ln\left(1 \pm e^{-x+\beta\mu}\right) \\ \text{integrate by parts} \\ = -\frac{2}{3}\int_0^\infty \mathrm{d}x\, x^{3/2} \frac{\mp e^{-x+\beta\mu}}{1 \pm e^{-x+\beta\mu}} \end{array}} = -\frac{2}{3} N k_{\rm B}T \frac{n_{\rm Q}}{n} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\mathrm{d}x\, x^{3/2}}{e^{x-\beta\mu} \pm 1}$$

$$\Rightarrow \boxed{\Phi = -\frac{2}{3} U}. \tag{16.42}$$

16.4.6. *Equation of State of a Quantum Ideal Gas*

Since $\Phi = -PV$ [see (14.73)], (16.42) implies that

$$\boxed{P = \frac{2}{3}\frac{U}{V}}, \tag{16.43}$$

i.e., *pressure is* 2/3 *energy density completely generally for a non-relativistic quantum ideal gas in 3D* [not just in the classical limit, cf. (1.29)].

**Exercise 16.4.** What happens in 2D? Trace back the way in which the dimensionality of space entered into all these calculations.

Using (16.41), we get the equation of state

$$\boxed{P = n k_{\rm B}T \left(\frac{2}{3}\frac{n_{\rm Q}}{n}\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\mathrm{d}x\, x^{3/2}}{e^{x-\beta\mu} \pm 1}\right)}, \tag{16.44}$$

where $\mu(n, T)$ is given by (16.32).

**Exercise 16.5.** Check that, in the classical limit, the expression in the brackets in (16.44) asymptotes to unity and the familiar classical equation of state (11.36) is thus recovered.

16.4.7. *Entropy and Adiabatic Processes*

Finally, using (16.20) and (16.42), we find

$$S = \frac{U - \Phi - \mu N}{T} = \frac{(5/3)U - \mu N}{T}, \qquad (16.45)$$

whence it follows that for an adiabatic process ($S = \text{const}$, $N = \text{const}$),

$$\boxed{PV^{5/3} = \text{const}}\,, \qquad (16.46)$$

again *completely generally for a non-relativistic gas in 3D.*

**Proof.** From (16.45), assuming $S = \text{const}$ and $N = \text{const}$,

$$\frac{S}{N} = \frac{5}{3}\frac{U}{NT} - \frac{\mu}{T} = \text{const}. \qquad (16.47)$$

But, from (16.41), $U/NT$ is a function of $\mu/T$ (equivalently, of $\beta\mu$) only because, according to (16.32), $n/n_{\rm Q}$ is a function of $\mu/T$ only. Therefore, in an adiabatic process,

$$\frac{\mu}{T} = \text{const}. \qquad (16.48)$$

But then, by (16.32),

$$\frac{n}{n_{\rm Q}} = \text{const} \quad \Rightarrow \quad n\lambda_{\rm th}^3 = \text{const} \quad \Rightarrow \quad VT^{3/2} = \text{const}, \qquad (16.49)$$

and, by (16.44),

$$\frac{P}{nk_{\rm B}T} = \text{const} \quad \Rightarrow \quad PVT^{-1} = \text{const}. \qquad (16.50)$$

Combining Eqs. (16.49) and (16.50), we get (16.46), q.e.d.

*NB:* While the exponent 5/3 turns out to be more general than the classical limit, it is *not* in general equal to $C_P/C_V$. The heat capacities have to be calculated, as usual, from (16.41) and (16.44) or by differentiating entropy (16.45) and will prove to have interesting temperature dependence for different types of quantum gases (see §§17.3, 18.2.2 and Exercise 17.2).

## 16.5. *Degeneration*

We have seen above (§16.4.3) that for $n\lambda_{\rm th}^3 \ll 1$ (hot, dilute gas), we recover the classical limit. Obviously, one would not go to all the trouble of calculating quantum statistics just to get back to the classical world. The new and exciting things will happen when the classical limit breaks down, viz., $n\lambda_{\rm th}^3 \gtrsim 1$.

Under what conditions does this happen? Let us start from the classical limit, use $P = nk_{\rm B}T$, and estimate:

$$n\lambda_{\rm th}^3 = \frac{P}{k_{\rm B}T}\hbar^3\left(\frac{2\pi}{mk_{\rm B}T}\right)^{3/2} \approx 2.5\cdot 10^{-5}\left(\frac{P}{1\ \text{atm}}\right)\left(\frac{T}{300\ \text{K}}\right)^{-5/2}\left(\frac{m}{m_{\rm p}}\right)^{-3/2}. \qquad (16.51)$$

This gives us

air at S.T.P.: $n\lambda_{\rm th}^3 \sim 10^{-6} \ll 1$, safely classical;

$^4$He at 4 K and 1 atm: $n\lambda_{\rm th}^3 \sim 0.15$, getting dangerous...;

electrons in metals: $n\lambda_{\rm th}^3 \sim 10^4 \gg 1$ at $T = 300$ K (here I used $n \sim 10^{28}$ m$^{-3}$, *not*

$n = P/k_B T$). Thus, they are completely degenerate even in everyday conditions! It does indeed turn out that you cannot correctly calculate heat capacity of metals solely based on classical models (see Exercise 19.2). This will be a clear application of Fermi statistics in the quantum (degenerate) limit.

Note that this teaches us that "low-" and "high-"temperature limits do not necessarily apply at temperatures naïvely appearing to be low or high from our everyday perspective. For example, for electrons in metals, temperature would stop being "low" (i.e., the classical limit would be approached) when $n\lambda_{\rm th}^3 \sim 1$, or $T \sim T_{\rm deg} \sim 2\pi n^{2/3}\hbar^2/m_e k_B \sim 10^4$ K. The "degeneration temperature" is high because density is high and the particles (electrons) are light. Of course most metals in fact would melt and, indeed, evaporate, dissociate, and ionise at such temperatures. Thus, the world is more quantum than you might have thought.

Another famous application of the theory of degenerate Fermi gases is to the admittedly less mundane environments of white dwarves and neutron stars, where densities are so high that even relativistic temperatures ($T \gtrsim mc^2/k_B$) can be "low" from the point of view of quantum effects being dominant (some elements of Chandrasekhar's theory of the stability of stars will appear in Exercise 17.1).

What is the physical meaning of degeneration? We have discussed this before.

In §11.9, I argued that $n\lambda_{\rm th}^3 \sim 1$ would mean that the number of quantum states available to a single particle ($\sim V/\lambda_{\rm th}^3$) would be comparable to the number of particles ($N$) and so it would cease to be the case that particles were unlikely to compete for the same microstates ($\bar{n}_i$'s are no longer small).

Even earlier, in §2.3.2, I put forward a somewhat more hand-waving (but perhaps, to some, more "physical") argument that, at low enough temperatures, the thermal spread in the particles' velocities would become so low that their positions would be completely blurred. The condition (2.29) that $T \gg T_{\rm deg}$ in order for the gas to be classical, which was derived on that basis, is the same as $n\lambda_{\rm th}^3 \ll 1$.

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**Exercise 16.6. Ultrarelativistic Quantum Gas.** Consider an ideal quantum gas (Bose or Fermi) in the ultrarelativistic limit and reproduce the calculations of §16.4 as follows.

(a) Find the equation that determines its chemical potential (implicitly) as a function of density $n$ and temperature $T$.

(b) Calculate the energy $U$ and grand potential $\Phi$ and hence prove that the equation of state can be written as

$$PV = \frac{1}{3}U, \qquad (16.52)$$

regardless of whether the gas is in the classical limit, degenerate limit or in between.

(c) Consider an adiabatic process with the number of particles held fixed and show that

$$PV^{4/3} = \text{const} \qquad (16.53)$$

for any temperature and density (not just in the classical limit, as in Exercise 11.4).

(d) Show that in the hot, dilute limit (large $T$, small $n$), $e^{\mu/k_B T} \ll 1$. Find the specific condition on $n$ and $T$ that must hold in order for the classical limit to be applicable. Hence derive the condition for the gas to cease to be classical and become degenerate.

(e) Estimate the minimum density for which an electron gas can be simultaneously degenerate and ultrarelativistic.

**Exercise 16.7. Pair Plasma.** At relativistic temperatures, the number of particles can stop being a fixed number, with production and annihilation of electron-positron pairs providing the number of particles required for thermal equilibrium. The reaction is

$$e^+ + e^- \Leftrightarrow \text{photon(s)}. \tag{16.54}$$

(a) What is the condition for the "chemical" equilibrium for this system?

(b) Assume that the numbers of electrons and positrons are the same (i.e., ignore the fact that there is ordinary matter and, therefore, a surplus of electrons). This allows you to treat the situation as fully symmetric and conclude that the chemical potentials of electrons and positrons are the same. What are they equal to? Hence calculate the density of electrons and positrons $n^\pm$ as functions of temperature, assuming $k_B T \gg m_e c^2$. You will need to know that

$$\int_0^\infty \frac{\mathrm{d}x\, x^2}{e^x + 1} = \frac{3}{2}\zeta(3), \quad \zeta(3) \approx 1.202 \tag{16.55}$$

(see, e.g., Landau & Lifshitz 1980, §58 for the derivation of this formula).

(c) To confirm the *a priori* assumption you made in (b), show that, at ultrarelativistic temperatures, the density of electrons and positrons will always be larger than the density of electrons in ordinary matter. This will require you to come up with a simple way of estimating the upper bound for the latter.

(d) Now consider the non-relativistic case, $k_B T \ll m_e c^2$, and assume that temperature is also low enough for the classical (non-degenerate) limit to apply. Let the density of electrons in matter, without pair production, be $n_0$. Show that, in equilibrium, the density of positrons due to spontaneous pair production is exponentially small:

$$n^+ \approx \frac{4}{n_0}\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^3 e^{-2m_e c^2/k_B T}. \tag{16.56}$$

*Hint.* Use the law of mass action (§15.4). Note that you can no longer assume that pairs are more numerous than ordinary electrons. The energy cost of producing an electron or a positron is $m_e c^2$.

**Exercise 16.8. Creation/Annihilation of Matter.** When the number of particles $N$ in an ideal gas is fixed, its chemical potential is determined implicitly from (16.32). Now, instead of fixing the number of particles, let us include them into the energy budget of our system (energy cost of making a particle is $mc^2$). How must the formula for $N$ be modified?

Using this new formula, calculate the number density of an ideal gas in equilibrium, at room temperature. Does this result adequately describe the room you are sitting in? If not, why do you think that is?

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## 17. Degenerate Fermi Gas

[Literature: Landau & Lifshitz (1980), §§57–58; Schrödinger (1990), Ch. VIII(a)]

Consider an ideal gas of fermions at very low $T$, so $\beta \to \infty$. Then (Fig. 25)

$$\frac{1}{e^{\beta(\varepsilon-\mu)} + 1} \to \begin{cases} 1 & \text{if } \varepsilon < \mu(T=0), \\ 0 & \text{if } \varepsilon > \mu(T=0). \end{cases} \tag{17.1}$$

So, at $T = 0$, the fermions "stack up" to occupy all the available single-particle states from the lowest-energy one to maximum energy equal to the value of the chemical potential at $T = 0$,

$$\varepsilon_F = \mu(T=0). \tag{17.2}$$

This is called the *Fermi energy*. The resulting "step-like" distribution is very simple, so we will be able to calculate everything quite easily.

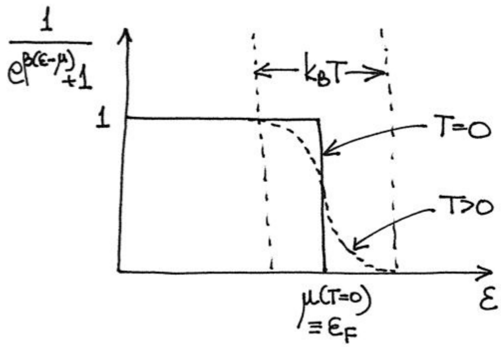


FIGURE 25. Fermi distribution at low $T$.

### 17.1. *Fermi Energy*

The first order of business is to calculate the chemical potential, or, in the parlance of Fermi-gas theory, the Fermi energy.

The number of particles contained in the "step" distribution is given by (16.31) [equivalently, by (16.32)] taken at $T = 0$, with the approximation (17.1):

$$N = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon) = \frac{2(2s+1)}{\sqrt{\pi}} \frac{V}{\lambda_{\text{th}}^3} \beta^{3/2} \underbrace{\int_0^{\varepsilon_F} d\varepsilon \sqrt{\varepsilon}}_{=\frac{2}{3}\varepsilon_F^{3/2}} = \frac{2(2s+1)Vm^{3/2}}{3\sqrt{2}\,\pi^2\hbar^3}\, \varepsilon_F^{3/2}. \tag{17.3}$$

Therefore, the Fermi energy of a Fermi gas of number density $n = N/V$ is

$$\boxed{\varepsilon_F = \frac{\hbar^2}{2m} \underbrace{\left(\frac{6\pi^2 n}{2s+1}\right)^{2/3}}_{\equiv k_F^2}}\,. \tag{17.4}$$

Apart from the numerical constants, this is dimensionally inevitable: there is nothing other than $n^{1/3}$ that we could have set the "Fermi wavenumber" to be proportional to.

This result tells us

—what the chemical potential at $T = 0$ is: $\mu(0) = \varepsilon_F$;

—what the maximum energy per particle at $T = 0$ is: $\varepsilon_F$;

—what the criterion is for treating the Fermi gas as a quantum gas at zero temperature: the width of the "step" in the distribution (Fig. 25) is $\sim k_B T$ and so the $T = 0$ limit applies to temperatures satisfying

$$T \ll T_F \equiv \frac{\varepsilon_F}{k_B} \sim \frac{\hbar^2 n^{2/3}}{m k_B} \sim T_{\text{deg}}, \tag{17.5}$$

precisely the degeneration temperature that I already derived in §§16.5, 11.9 and 2.3.2 (e.g., $T_F \sim 10^4$ K for electrons in metals).

*NB:* I stress again that "low $T$" in this context just means $T \ll T_F$, even though $T_F$ can be very high for systems with large density and low particle mass. For example, for electrons in white dwarves (Exercise 17.1), $\varepsilon_F \sim$ MeV and so $T_F \sim 10^{10}$ K $\sim m_e c^2$, so in fact they are not just hot but relativistically hot—and all our calculations must be redone with the relativistic formula for $\varepsilon(k)$ [see (16.24)].

### 17.2. *Mean Energy and Equation of State at $T = 0$*

Moving on to calculate the mean energy (16.41), we get

$$\frac{U}{N} = \frac{\int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\varepsilon}{\int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)} = \frac{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon^{3/2}}{\int_0^{\varepsilon_F} d\varepsilon \sqrt{\varepsilon}} = \frac{3}{5}\,\varepsilon_F \quad \Rightarrow \quad \boxed{U = \frac{3}{5}\,N\varepsilon_F} \tag{17.6}$$

Hence the equation of state (16.43) is

$$\boxed{P = \frac{2}{3}\frac{U}{V} = \frac{2}{5}\,n\varepsilon_F = \frac{\hbar^2}{5m}\left(\frac{6\pi^2}{2s+1}\right)^{2/3} n^{5/3}}\,. \tag{17.7}$$

This is, of course, independent of $T$ (indeed, $T = 0$) and so the gas might be said to behave as a "pure mechanism" (changes in volume and pressure are hard-coupled, with no heat exchange involved).

Note that (17.7) is equivalent to $PV^{5/3} = \text{const}$, the general adiabatic law (16.46) for a quantum gas. This is not surprising as we are at $T = 0$ and expect $S = 0 = \text{const}$ (although I will only prove this in the next section).

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**Exercise 17.1. White Dwarves, Neutron Stars and Black Holes.** This question deals with the states into which stars collapse under gravity when they run out of nuclear fuel. As matter is compressed, the density of electrons will eventually become so large as to turn them into a degenerate gas, effectively at zero temperature, while the nuclei supply gravity and enforce charge neutrality (any local deviation from zero charge density is quickly ironed out by large electric forces). Let us assume that the total mass of matter per electron is $m$ (typically, for each electron, there is one proton and roughly one neutron, so $m \approx m_e + m_p + m_n \approx 2m_n$). Our objective is, given the total mass $M$ of the star, to determine its radius $R$. They are related by

$$M = 4\pi \int_0^R dr r^2 \rho(r), \tag{17.8}$$

where $\rho(r) = mn_e(r)$ is the mass density and $n_e(r)$ is the electron number density. Thus, we need to work out the density profile of a spherically symmetrical cloud of degenerate ($T = 0$) electron gas in a gravitational field determined by that same density profile, the gravitational potential $\varphi$ satisfying

$$\nabla^2\varphi = 4\pi G\rho. \tag{17.9}$$

(a) Assuming particle equlibrium and arguing that the effective potential energy associated with placing an electron at the location $r$ is $m\varphi(r)$ (cf. §14.5), show that the Fermi energy (which is the chemical potential at $T = 0$ and without the contribution from gravitational potential energy) of the electron gas can be expressed as

$$\varepsilon_F(r) = \frac{1}{R^4\Lambda^2} f\left(\frac{r}{R}\right), \quad \text{where} \quad \Lambda = \frac{8\sqrt{2}Gm^2 m_e^{3/2}}{3\pi\hbar^3}, \tag{17.10}$$

and $f(x)$ is a dimensionless function of a dimensionless argument satisfying the boundary-value problem

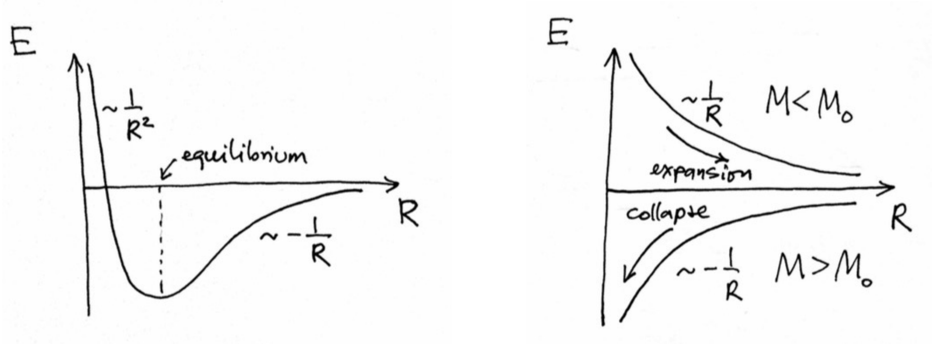
$$-\frac{1}{x^2}\frac{d}{dx}x^2\frac{df}{dx} = f^{3/2}, \quad f(1) = 0, \quad f'(0) = 0. \tag{17.11}$$

While this equation can only be solved numerically, you should not find it a difficult task to sketch its solution. Sketch also the resulting density profile.

(b) On the basis of (17.8) and (17.10), argue (dimensionally) that the radius of a white dwarf $R \propto M^{-1/3}$. Indeed, using (17.9), you should be able to show precisely that

$$MR^3 = -\frac{f'(1)}{mG\Lambda^2}. \tag{17.12}$$

Numerical solution of (17.11) gives $f'(1) \approx -132$. Hence show that the radius of a solar-mass white dwarf ($M_\odot \approx 2 \cdot 10^{30}$ kg) is of the order of the radius of the Earth.




(a) non-relativistic; see (17.13) (b) relativistic; see (17.14)

FIGURE 26. Energy of a white dwarf (or neutron star).

The existence of this equilibrium solution is easy to interpret. The gravitational energy pulling the white dwarf together is, obviously, $\propto -M^2/R$, whereas the internal (Fermi) energy pushing it apart is $\propto N(N/V)^{2/3} \propto M^{5/3}/R^2$. Their sum, the total energy

$$E = \text{const}\frac{M^{5/3}}{R^2} - \text{const}\frac{M^2}{R} \tag{17.13}$$

has a minimum at $R \propto M^{-1/3}$, where the equlibrium solution will sit (Fig. 26a). Equivalently, this is a balance between gravity and pressure.

The situation changes if the electron gas is ultrarelativistic: the Fermi energy is then $\propto N(N/V)^{1/3} \propto M^{4/3}/R$ (see Exercise 17.4), which has the same $R$ dependence as the gravitational energy and so can only be balanced with the latter at a single value of $M = M_0$, at which the total energy

$$E = \text{const}\frac{M^{4/3}}{R} - \text{const}\frac{M^2}{R} \tag{17.14}$$

is zero. When $M < M_0$, $E > 0$, so the gas will want to expand until it becomes non-relativistic; when $M > M_0$, it will contract to ever smaller $R$ (Fig. 26b). In the next part of this Exercise, we discover how this result is reflected in a formal calculation.

(c) Show that the non-relativistic approximation ($\varepsilon_{\rm F} \ll m_e c^2$) breaks down for

$$M \gtrsim \frac{1}{m^2}\left(\frac{c\hbar}{G}\right)^{3/2}. \tag{17.15}$$

For this estimate, you may use the mean density $3M/4\pi R^3$ of the white dwarf or the density at its centre; if you use the latter, you will need to know that $f(0) \approx 178$ (how different are the mean density and the density at the centre?). How does the mass threshold that you have obtained compare with the mass of our Sun?

(d) Redo the above calculations for an ultrarelativistic gas and show that

$$\varepsilon_{\rm F}(r) = \frac{1}{R\sqrt{\Lambda}} f\left(\frac{r}{R}\right), \quad \text{where} \quad \Lambda = \frac{4Gm^2}{3\pi c^3\hbar^3} \quad \text{and} \quad -\frac{1}{x^2}\frac{\mathrm{d}}{\mathrm{d}x}x^2\frac{\mathrm{d}f}{\mathrm{d}x} = f^3 \tag{17.16}$$

(with the same boundary conditions as before). Show that there is a single value of mass, $M = M_0$, compatible with such an equilibrium. Using the fact (which can be obtained numerically) that $f'(1) \approx -2$, show that $M_0 \approx 1.45 M_\odot$. This is called the *Chandrasekhar limit* (he discovered it at the age of 19, during his voyage from India to England in 1930).

As explained above, when $M > M_0$, the white dwarf collapses. As density goes up, electrons are captured by protons and everything turns into neutrons. The result is again a Fermi gas, but now consisting of neutrons. If its Fermi energy is smaller than $m_n c^2$, the non-relativistic calculation done in (a)–(b) applies, but with $m_e \to m_n$ and $m \to m_n$. The stable solution obtained this way is called a *neutron star*. For masses large enough that neutrons become relativistic, this too is unstable and collapses into a *black hole*. The corresponding mass limit is a few solar masses. You may estimate it yourself, working in the same vein as you did in (c)–(d). Note, however, that things are, in fact, more complicated: as neutrons become relativistic, Newton's equation (17.9) is no longer valid, you have to use GR and also work with the general relativistic energy-momentum relation (16.23) because the ultrarelativistic limit is, in fact, never quite reached. The quantitative details are messy, but the qualitative conclusion is the same: there is an order-unity interval of masses around $M_\odot$ in which neutron stars can exist; ligher stars end up white dwarves, heavier ones collapse into black holes.

[Literature: Landau & Lifshitz (1980), Ch. XI]

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## 17.3. *Heat Capacity*

Our construction of the thermodynamics of Fermi gas at low temperature is not complete because knowing $U$ at $T = 0$ does not help us calculate the heat capacities, which require knowledge of the derivative of $U$ (or of $S$) with respect to $T$.[67] Clearly, at $T \ll \varepsilon_F/k_B$, the mean energy must be expressible as

$$U(T) = \underbrace{U(T=0)}_{=\frac{3}{5}\varepsilon_F N} + \delta U(T), \tag{17.17}$$

where $\delta U(T)$ is a small correction, which completely determines the heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial \delta U}{\partial T}\right)_V. \tag{17.18}$$

I will calculate $\delta U(T)$ systematically in §17.3.3 (see footnote 21 regarding why you ought to read that section), but first let me give a qualitative argument that elucidates the meaning of the answer.

### 17.3.1. *Qualitative Calculation*

At small but non-zero $T \ll \varepsilon_F/k_B$, the Fermi distribution still has a step-like shape, but the step is not sharp at $\varepsilon = \varepsilon_F$: it is slightly worn and has a width (obviously) of order $\Delta\varepsilon \sim k_B T$ (Fig. 25). This means that a small number of fermions with energies $\sim \varepsilon_F$ can be kicked out of the ground state to slightly higher energies. This number is

$$\Delta N_{\text{excited}} \sim g(\varepsilon_F)\Delta\varepsilon \sim g(\varepsilon_F) k_B T. \tag{17.19}$$

Each of these fermions will have on the order of $\Delta\varepsilon \sim k_B T$ more energy than it would have had at $T = 0$. Therefore, the excess mean energy compared to the $T = 0$ state will be

$$\delta U(T) \sim \Delta N_{\text{excited}} \Delta\varepsilon \sim g(\varepsilon_F)(k_B T)^2 \sim \frac{N(k_B T)^2}{\varepsilon_F}, \tag{17.20}$$

where I have estimated the density of states at Fermi energy simply as $g(\varepsilon_F) \sim N/\varepsilon_F$ because $N = \int_0^{\varepsilon_F} \mathrm{d}\varepsilon\, g(\varepsilon)$ at $T = 0$.

Thus, the finite-$T$ correction to energy (17.20) is quadratic in $T$, and we find

$$\boxed{C_V = \left(\frac{\partial \delta U}{\partial T}\right)_V = \text{const}\, N k_B \frac{k_B T}{\varepsilon_F}}. \tag{17.21}$$

Therefore, the heat capacity starts off linear with $T$ at low $T$ and eventually asymptotes

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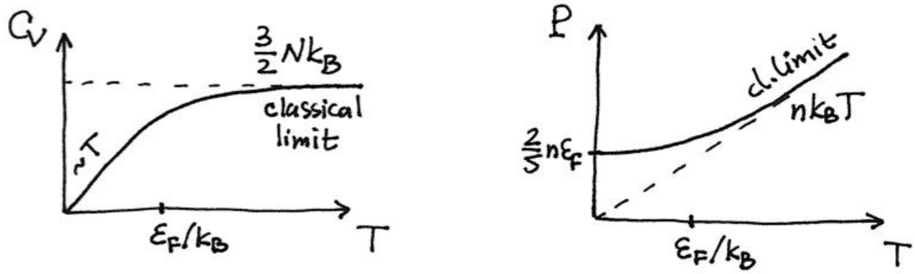
[67] Note that we have not even proven yet that $S = 0$ at $T = 0$: in (16.45), the numerator and the denominator are both 0 at $T = 0$, but finding the limit of their ratio requires knowledge of the derivatives of $U$ and $\mu$ with respect to $T$.




(a) Heat capacity $C_V(T)$; see (17.28) (b) Equation of state $P(T)$; see (17.29)

FIGURE 27. Thermodynamics of a Fermi gas.

to a const ($= 3Nk_B/2$) at high $T$ (Fig. 27a). In metals at sufficiently low temperatures, this heat capacity due to electrons is the dominant contribution because the heat capacity due to lattice vibrations is $\propto T^3$ (see Exercise 19.2).

### 17.3.2. *Equation of State at* $T > 0$

The estimate (17.20), via $P = (2/3)U/V$ [see (16.43)], also gives us the general form of the equation of state for a Fermi gas at low temperatures: $P$ grows quadratically from the $T = 0$ value [see (17.7)], asymptoting to $P = nk_BT$ at $T \gg \varepsilon_F$ (Fig. 27b).

This highlights a key thermodynamical (and, indeed mechanical) difference between Fermi gas and classical gas: *at low T, the Fermi gas exerts a much larger pressure than it would have done had it been classical.* This is of course due to the stacking of particles in the energy levels up to $\varepsilon_F$ and the consequent larger energy density than would have been achieved at low temperature had Pauli's exclusion principle not been in operation.

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### 17.3.3. *Quantitative Calculation: Sommerfeld Expansion*

To calculate the constant in (17.21), we need to develop a more quantitative theory, namely, carry out an expansion of the integrals in (16.31) and (16.41) in the small parameter $k_BT/\varepsilon_F = 1/\varepsilon_F\beta \ll 1$. In order to do this, we will require some maths: we must learn how to calculate integrals of the form

$$I = \int_0^\infty \frac{d\varepsilon\, f(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}, \tag{17.22}$$

where $f(\varepsilon) = g(\varepsilon) \propto \sqrt{\varepsilon}$ in (16.31), $f(\varepsilon) = g(\varepsilon)\varepsilon \propto \varepsilon^{3/2}$ in (16.41), and it can also scale with other powers of $\varepsilon$ in other limits and regimes (e.g., in 2D, or for the ultrarelativistic calculations in Exercise 17.4).

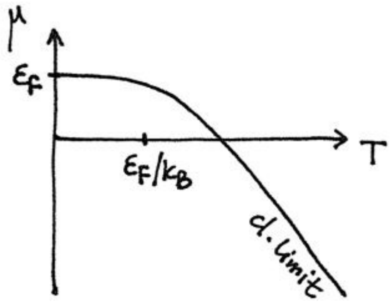



FIGURE 28. Chemical potential $\mu(T)$ of a Fermi gas; see (17.25).

We start by changing the integration variable to $x = \beta(\varepsilon - \mu)$, so $\varepsilon = \mu + k_{\rm B}Tx$. Then

$$
\begin{aligned}
I &= k_{\rm B}T \int_{-\mu/k_{\rm B}T}^{\infty} \frac{{\rm d}x\, f(\mu + k_{\rm B}Tx)}{e^x + 1} \\
&= k_{\rm B}T \int_0^\infty \frac{{\rm d}x\, f(\mu + k_{\rm B}Tx)}{e^x + 1} + \underbrace{k_{\rm B}T \int_0^{\mu/k_{\rm B}T} \frac{{\rm d}x\, f(\mu - k_{\rm B}Tx)}{e^{-x} + 1}}_{\substack{\text{changed } x \to -x,\\ \text{now use}\\ \frac{1}{e^{-x}+1} = 1 - \frac{1}{e^x+1}}} \\
&= \underbrace{k_{\rm B}T \int_0^{\mu/k_{\rm B}T} {\rm d}x\, f(\mu - k_{\rm B}Tx)}_{\substack{\text{change variable back}\\ \text{to } \varepsilon = \mu - k_{\rm B}Tx}} + k_{\rm B}T \left[ \int_0^\infty \frac{{\rm d}x\, f(\mu + k_{\rm B}Tx)}{e^x + 1} - \underbrace{\int_0^{\mu/k_{\rm B}T} \frac{{\rm d}x\, f(\mu - k_{\rm B}Tx)}{e^x + 1}}_{\substack{\text{take } \mu/k_{\rm B}T \to \infty \text{ in the}\\ \text{upper limit of}\\ \text{integration, pick up only}\\ \text{exponentially small}\\ \text{error because}\\ k_{\rm B}T \ll \varepsilon_{\rm F} \sim \mu}} \right] \\
&\approx \int_0^\mu {\rm d}\varepsilon\, f(\varepsilon) + k_{\rm B}T \int_0^\infty \frac{{\rm d}x}{e^x + 1} \underbrace{\left[ f(\mu + k_{\rm B}Tx) - f(\mu - k_{\rm B}Tx) \right]}_{= 2k_{\rm B}Tx f'(\mu) + O\left[(k_{\rm B}Tx)^3\right]} \\
&= \int_0^\mu {\rm d}\varepsilon\, f(\varepsilon) + 2(k_{\rm B}T)^2 f'(\mu) \underbrace{\int_0^\infty \frac{{\rm d}x\, x}{e^x + 1}}_{= \frac{\pi^2}{12}} + O\left[ \left( \frac{k_{\rm B}T}{\mu} \right)^4 \right] \\
&= \int_0^\mu {\rm d}\varepsilon\, f(\varepsilon) + \frac{\pi^2}{6} f'(\mu) (k_{\rm B}T)^2 + \dots
\end{aligned}
\tag{17.23}
$$

This is called the *Sommerfeld expansion*. It allows us to calculate finite-$T$ corrections to anything we like by substituting the appropriate form of $f(\varepsilon)$.

First, we calculate the chemical potential from (16.31), to which we apply (17.23) with

$$
f(\varepsilon) = g(\varepsilon) = \frac{N}{(2/3)\varepsilon_{\rm F}^{3/2}} \sqrt{\varepsilon}. \tag{17.24}
$$

This gives

$$N = \frac{N}{(2/3)\varepsilon_F^{3/2}}\left[\frac{2}{3}\mu^{3/2} + \underbrace{\frac{\pi^2}{6}\frac{1}{2\sqrt{\mu}}}_{\mu=\varepsilon_F+\dots}(k_B T)^2 + \dots\right] \quad\Rightarrow\quad \boxed{\mu = \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \dots\right]}. \tag{17.25}$$

Thus, $\mu$ falls off with $T$—eventually, it must become large and negative in the classical limit, as per (16.35) (Fig. 28).

Now we turn to mean energy: in (16.41), use (17.23) with

$$f(\varepsilon) = g(\varepsilon)\varepsilon = \frac{N}{(2/3)\varepsilon_F^{3/2}}\,\varepsilon^{3/2} \tag{17.26}$$

to get

$$U = \frac{N}{(2/3)\varepsilon_F^{3/2}}\left[\underbrace{\frac{2}{5}\mu^{5/2}}_{\text{use (17.25)}} + \underbrace{\frac{\pi^2}{6}\frac{3}{2}\sqrt{\mu}}_{\mu=\varepsilon_F+\dots}(k_B T)^2 + \dots\right] = \frac{3}{5}N\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \dots\right]. \tag{17.27}$$

In the lowest order, this gives us back (17.6), while the next-order correction is precisely the $\delta U(T)$ that we need to calculate heat capacity:

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = N k_B \frac{\pi^2}{2}\frac{k_B T}{\varepsilon_F} + \dots}. \tag{17.28}$$

The constant promised in (17.21) is, thus, $\pi^2/2$.

The approximation (17.27) immediately gives us the equation of state:

$$\boxed{P = \frac{2}{3}\frac{U}{V} = \frac{2}{5}n\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \dots\right]}. \tag{17.29}$$

Finally, substituting (17.25) and (17.27) into (16.45), we find the entropy of a Fermi gas at low temperature:

$$\boxed{S = \frac{1}{T}\left(\frac{5}{3}U - \mu N\right) = N k_B \frac{\pi^2}{2}\frac{k_B T}{\varepsilon_F} + \dots \to 0 \quad \text{as} \quad T \to 0}. \tag{17.30}$$

---

**Exercise 17.2. Ratio of Heat Capacities for a Fermi Gas.** Show that the ratio of heat capacities for a Fermi gas $C_P/C_V \to 1$ as $T \to 0$. Can you show this without the need to use the detailed calculation of §17.3.3? Sketch $C_P/C_V$ as a function of $T$ from $T = 0$ to the high-temperature limit.

**Exercise 17.3.** We have seen that $\mu > 0$ for a Fermi gas at low temperatures. In §14.2, we argued, on the basis of (14.21), that adding particles to a system (at constant $U$ and $V$) would increase entropy and so $\mu$ would have to be negative. Why does this line of reasoning fail for a degenerate Fermi gas?

**Exercise 17.4. Heat Capacity of an Ultrarelativistic Electron Gas.** Find the Fermi energy $\varepsilon_F$ of an ultrarelativistic electron gas and show that when $k_B T \ll \varepsilon_F$, its energy density is

$$\frac{U}{V} = \frac{3}{4}n\varepsilon_F \tag{17.31}$$

and its heat capacity is

$$C_V = N k_B \pi^2 \frac{k_B T}{\varepsilon_F}. \tag{17.32}$$

Sketch the heat capacity $C_V$ of an ultrarelativistic electron gas as a function of temperature, from $T \ll \varepsilon_{\rm F}/k_{\rm B}$ to $T \gg \varepsilon_{\rm F}/k_{\rm B}$.

**Exercise 17.5. Paramagnetism of a Degenerate Electron Gas (Pauli Magnetism).** Consider a fully degenerate non-relativistic electron gas in a weak magnetic field. Since the electrons have two spin states (up and down), take the energy levels to be

$$\varepsilon(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2m} \pm \mu_B B, \tag{17.33}$$

where $\mu_B = e\hbar/2m_e c$ is the Bohr magneton. Assume the field to be sufficiently weak so that $\mu_B B \ll \varepsilon_{\rm F}$

(a) Show that the magnetic susceptibility of this system is

$$\chi \equiv \left(\frac{\partial M}{\partial B}\right)_{B=0} = \frac{3^{1/3}}{4\pi^{4/3}}\frac{e^2}{m_e c^2}\,n^{1/3}, \tag{17.34}$$

where $M$ is the magnetisation (total magnetic moment per unit volume) and $n$ the number density. *Hint.* Express $M$ in terms of the grand potential $\Phi$. Then use the fact that energy enters the Fermi statistics in combination $\varepsilon - \mu$ with the chemical potential $\mu$. Therefore, in order to calculate the individual contributions from the spin-up and spin-down states to the integrals over single-particle states, you can use the unmagnetised formulae with $\mu$ replaced by $\mu \pm \mu_B B$, viz., the grand potential, for example, is

$$\Phi(\mu, B) = \frac{1}{2}\,\Phi_0(\mu + \mu_B B) + \frac{1}{2}\,\Phi_0(\mu - \mu_B B), \tag{17.35}$$

where $\Phi_0(\mu) = \Phi(\mu, B = 0)$ is the grand potential in the unmagnetised case. Make sure to take full advantage of the fact that $\mu_B B \ll \varepsilon_{\rm F}$.

(b) Show that in the classical (non-degenerate) limit, the above method recovers Curie's law. Sketch $\chi$ as a function of $T$, from very low to very high temperatures.

(c) Show that at $T \ll \varepsilon_{\rm F}/k_B$, the finite-temperature correction to $\chi$ is quadratic in $T$ and negative (i.e., $\chi$ goes down as $T$ increases).

---

## 18. Degenerate Bose Gas

[Literature: Landau & Lifshitz (1980), §62; Schrödinger (1990), Ch. VIII(b)]

The strangeness of the degenerate Fermi gas, compared to classical gas, was, in a sense, that it behaved as if there were more of it than there actually was (§17.3.2). The strangeness of the degenerate Bose gas will be that it behaves as if there were less of it.

### 18.1. *Bose-Einstein Condensation*

Let us recall [see (16.14)] that for an ideal gas of bosons,

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1} \tag{18.1}$$

and multiple particles are welcome to occupy the same quantum state. The above expression requires $\mu < \varepsilon_i$ for all single-particle states $i$, otherwise we would get unphysical values $\bar{n}_i < 0$. Therefore,[68]

$$\mu < \min(\varepsilon_i) = \varepsilon_0 = 0. \tag{18.2}$$

[68] I will assume here that the lowest-energy state has zero energy (e.g., for ideal gas, $\varepsilon = \hbar^2 k^2/2m = 0$ for $k = 0$), but it is easy to adjust the theory to the case $\varepsilon_0 \neq 0$ (as, e.g., in a magnetised Bose gas; see Exercise 18.3).

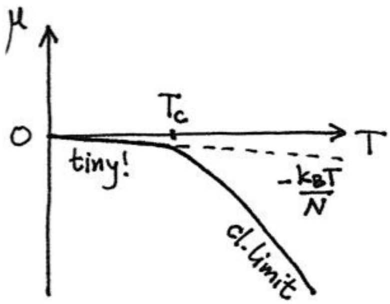



FIGURE 29. Chemical potential $\mu(T)$ of a Bose gas; see (18.4).

Clearly, as $T \to 0$ ($\beta \to \infty$), the lower is the energy the larger is the occupation number and so at $T = +0$ we expect all particles to drop to the ground state:

$$\bar{n}_0 = \frac{1}{e^{-\beta\mu} - 1} \to N \quad \text{as} \quad \beta \to \infty \tag{18.3}$$

$$\Rightarrow \quad \mu(T \to +0) \approx -k_B T \ln\left(1 + \frac{1}{N}\right) \approx -\frac{k_B T}{N} \to -0. \tag{18.4}$$

The chemical potential of a Bose gas starts off at $\mu = 0$, eventually decaying further with increasing $T$ to its classical value (16.35) (Fig. 29).

Thus, at low temperatures, *the lowest-energy state becomes macroscopically occupied:* $\bar{n}_0(T = 0) = N$ and, clearly, $\bar{n}_0 \sim$ some significant fraction of $N$ for $T$ just above zero. This is a serious problem for the calculations in §16.4, which were all done in the continuous limit. Indeed, in (16.30), we replaced the sum over states $i$ with an integral over energies weighted by the density of states, but the latter was $g(\varepsilon) \propto \sqrt{\varepsilon}$ [see (16.29)], so the $\varepsilon = 0$ state always gave us a vanishing contribution to our integrals! This is not surprising as the continuous approximation of a sum over states can obviously only be reasonable if the number of particles in each state is small compared to their total number $N$. As we have just seen, this is patently wrong for a Bose gas at sufficiently low $T$, so we must adjust our theory. In order to adjust it, let us first see how, mathematically speaking, it breaks down as $T \to 0$.

Recall that the first step in any treatment of a quantum gas is to calculate $\mu(n, T)$ from (16.32), a transcendental equation that has the form, for a Bose gas,

$$f(\beta\mu) \equiv \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\mathrm{d}x\sqrt{x}}{e^{x-\beta\mu} - 1} = \frac{n}{n_Q} \propto \frac{n}{T^{3/2}}. \tag{18.5}$$

The solution to this equation (see Fig. 30) certainly exists at low $n$ and high $T$ (small right-hand side)—that was the classical limit (§16.4.3). The solution is there because in the limit $\beta\mu \to -\infty$, the function $f(\beta\mu) \approx e^{\beta\mu}$ is monotonic and one can always find the value of $\mu$ for which (18.5) would be satisfied. The solution also always exists in the opposite (low-$T$) limit for Fermi gases, with $\mu(T \to 0)$ being the Fermi energy: again, this is because, in the limit $\beta\mu \to \infty$, the Fermi version of our function $f(\beta\mu) \approx (2/\sqrt{\pi}) \int_0^{\beta\mu} \mathrm{d}x\sqrt{x} = (4/3\sqrt{\pi})(\beta\mu)^{3/2}$ [this is (17.3), $\mu = \varepsilon_F$] is monotonic. In contrast, for Bose gas, as we saw in (18.2), there are no physically legitimate positive values of $\mu$ and so $f(\beta\mu)$ has a finite upper limit:

$$f(\beta\mu) \leqslant f(0) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\mathrm{d}x\sqrt{x}}{e^x - 1} = \zeta\left(\frac{3}{2}\right) \approx 2.612, \tag{18.6}$$

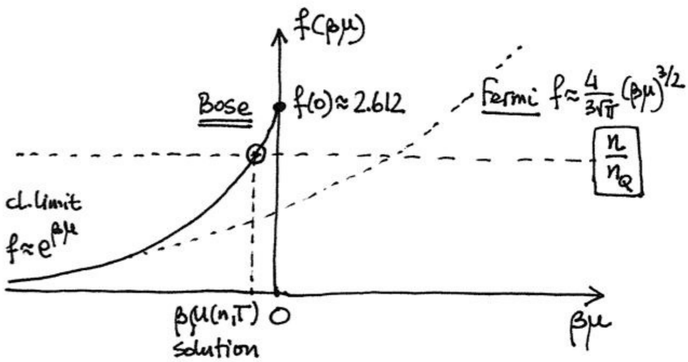



FIGURE 30. Solving (18.5) for $\mu(n,T)$ of a Bose gas.

where $\zeta$ is Riemann's zeta function (it does not matter how the integral is calculated, the important thing is that it is a finite number).

Therefore, if $n/n_Q > f(0)$ (and there is no reason why that cannot be, at low enough $T$ and/or high enough $n$), (18.5) no longer has a solution! The temperature below which this happens is $T = T_c$ such that

$$\frac{n}{n_Q} = \frac{n\lambda_{th}^3}{2s+1} = f(0) \approx 2.612 \quad \Rightarrow \quad \boxed{T_c \approx \frac{2\pi\hbar^2}{mk_B}\left[\frac{n}{2.612(2s+1)}\right]^{2/3}}. \tag{18.7}$$

Thus,

<u>for $T > T_c$</u>, all is well and we can always find $\mu(n,T)$; as $T \to T_c + 0$, we will have $\mu \to -0$;

<u>for $T < T_c$</u>, we must set $\mu = 0$,[69] but this means that now (18.5) no longer determines $\mu$, but rather the number of particles in the excited states ($\varepsilon > 0$):

$$N_{excited} = n_Q V f(0) < N. \tag{18.8}$$

Equivalently,

$$\boxed{\frac{N_{excited}}{N} \approx \frac{2.612(2s+1)}{n\lambda_{th}^3} = \left(\frac{T}{T_c}\right)^{3/2}}, \tag{18.9}$$

whence the occupation number of the ground state is

$$\boxed{\bar{n}_0 = N - N_{excited} = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]}. \tag{18.10}$$

The ground state is macroscopically occupied at $T < T_c$ and $\bar{n}_0 = N$ at $T = 0$ (Fig. 31).

The phenomenon of a macroscopic number of particles collecting in the lowest-energy state is called *Bose–Einstein condensation*. This is a kind of phase transition (which occurs at $T = T_c$), but the condensation is not like ordinary condensation of vapour: it occurs in the momentum space! When the condensate is present ($T < T_c$), *Bose gas behaves as a system in which the number of particles is not conserved* at all because particles can always leave the excited population ($N_{excited}$) and drop into the condensate ($\bar{n}_0$),

[69]From (18.4), we know that it is a tiny bit below zero, but for the purposes of the continuous approximation, this is 0, because $N \ggg\ggg 1$ in the thermodynamic limit.

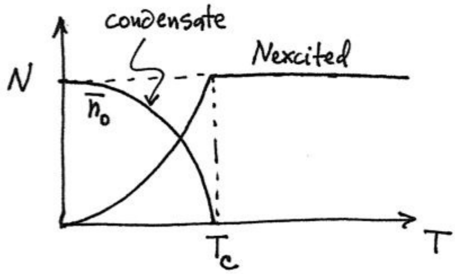



FIGURE 31. Excited particles ($N_{\rm excited}$) and the condensate ($\bar{n}_0$).

or vice versa, and the number of the excited particles is determined by thermodynamical parameters (temperature and total mean density). This is rather similar to the way a photon gas behaves in the sense that for the latter too, the number of photons is set by the temperature (mean energy) of the system and, appropriately, $\mu = 0$, a generic feature of systems in which the number of particles is not conserved (see §19 and Exercise 19.1).[70]

As might have been expected, the critical temperature $T_{\rm c} \sim T_{\rm deg}$, the degeneration temperature (i.e., at $T \gg T_{\rm c}$, we are back in the classical limit). For $^4$He, $T_{\rm c} \approx 3$ K, quite cold, and this is a typical value under normal conditions, so not many gases are still gases at these temperatures and Bose condensates tend to be quite exotic objects.[71] In 2001, Cornell, Wieman and Ketterle got the Nobel Prize for the first experimental observation of Bose condensation, one of those triumphs of physics in which mathematical reasoning predicting strange and whimsical phenomena is proven right as those strange and whimsical phenomena are found to be real. We have become used to this, but do pause and ponder what an extraordinary thing this is.

---

**Exercise 18.1. Low Energy Levels in Degenerate Bose Gas.** In a degenerate Bose gas, the lowest energy level (particle energy $\varepsilon_0 = 0$) is macroscopically occupied, in the sense that its occupation number $\bar{n}_0$ is comparable to the total number of particles $N$. Is the first energy level (particle energy $\varepsilon_1$, the next one above the lowest) also macroscopically occupied? In order to answer this question, estimate the occupation number of the first level and work out how it scales with $N$ (you will find that $\bar{n}_1 \propto$ a fractional power of $N$). What is the significance of this result: do the particles in the first level require special consideration as a condensate the same way the zeroth-level ones did?

---

## 18.2. *Thermodynamics of Degenerate Bose Gas*

The salient fact here is that the thermodynamics of Bose gas at $T < T_{\rm c}$ is decided by the particles that are *not* in the condensate (which is energetically invisible). So this is the thermodynamics of a gas with variable number of particles, which can come out of the condensate or drop back into it, depending on $T$.

---

[70] Another system of this ilk is ultrarelativistic pair plasma, which you encountered in Exercise 16.7.

[71] Superfluidity and and superconductivity are related phenomena, although the systems involved are not really non-interacting ideal gases and one needs to do quite a bit more theory to understand them (see, e.g., Lifshitz & Pitaevskii 1980).

18.2.1. *Mean Energy*

Using the results obtained in the continuous approximation (which is fine for the excited particles), we get, from (16.41) at $T < T_c$ and, therefore, with $\mu = 0$,

$$U = \frac{(2s+1)V}{\lambda_{\rm th}^3} k_{\rm B}T \underbrace{\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{{\rm d}x\, x^{3/2}}{e^x - 1}}_{\substack{= (3/2)\zeta(5/2) \\ \approx (3/2)\cdot 1.341}} \approx \underbrace{\frac{3\cdot 1.341}{2(2\pi)^{3/2}}}_{\approx 0.128} \frac{(2s+1)Vm^{3/2}}{\hbar^3}(k_{\rm B}T)^{5/2}. \quad (18.11)$$

In view of (18.7),

$$\frac{(2s+1)Vm^{3/2}}{\hbar^3(2\pi)^{3/2}} \approx \frac{N}{2.612(k_{\rm B}T_c)^{3/2}}, \quad (18.12)$$

where $N$ is the *total* number of particles. Substituting this into (18.11), we can rewrite the latter equation in the following form:

$$\boxed{U \approx 0.77 N k_{\rm B} T_c \left(\frac{T}{T_c}\right)^{5/2}}. \quad (18.13)$$

Note, however, that (18.11) perhaps better emphasises the fact that the mean energy depends on $T$ and $V$, but *not* on the number of particles (as the subset of excited particles is adjustable by the system depending on what volume the particles are called upon to occupy and at what temperature they are doing it).

18.2.2. *Heat Capacity*

We can now calculate the heat capacity:

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{5}{2}\frac{U}{T} \approx 1.93 N k_{\rm B} \left(\frac{T}{T_c}\right)^{3/2}}. \quad (18.14)$$

Note that $1.93 > 3/2$, so $C_V$ at $T = T_c$ is larger than it is in the classical limit. It turns out that at $T = T_c$, $C_V$ has a maximum and a discontinuous derivative (Fig. 32a). The jump in the derivative can be calculated by expanding around $T = T_c$. This is done, e.g., in Landau & Lifshitz (1980, §62). The answer is

$$\left.\frac{\partial C_V}{\partial T}\right|_{T=T_c-0} \approx 2.89\, \frac{N k_{\rm B}}{T_c}, \quad (18.15)$$

$$\left.\frac{\partial C_V}{\partial T}\right|_{T=T_c+0} \approx -0.77\, \frac{N k_{\rm B}}{T_c}. \quad (18.16)$$

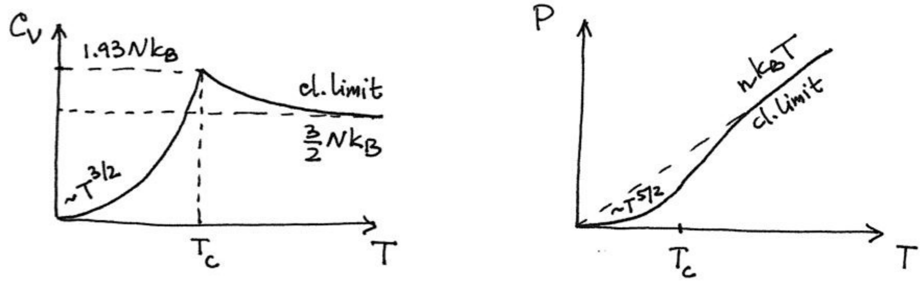
Thus, Bose condensation is a *3rd-order phase transition* (meaning that a third derivative of $\Phi$ is discontinuous).

18.2.3. *Equation of State*

As usual, the grand potential is $\Phi = -PV = -(2/3)U$ and so the equation of state is

$$\boxed{P \approx 0.085\, \frac{(2s+1)m^{3/2}}{\hbar^3}(k_{\rm B}T)^{5/2} \approx 0.51 n k_{\rm B} T_c \left(\frac{T}{T_c}\right)^{5/2}}. \quad (18.17)$$

The salient fact here is that *pressure (equivalently, energy density) of the gas is independent of particle density and depends on temperature only*. Obviously, at $T \gg T_c$, the equation of state must asymptote to the classical ideal-gas law (Fig. 32b).




(a) Heat capacity $C_V(T)$; see (18.14), (18.15) and (18.16)

(b) Equation of state $P(T)$; see (18.17)

FIGURE 32. Thermodynamics of a Bose gas.

As I promised at the beginning of §18, a degenerate Bose gas exerts less pressure at low $T$ than it would have done had it been classical (in contrast to Fermi gas, which punches above its weight; §17.3.2). This is, of course, again because of the energetic invisibility of the part of the gas that has dropped into the Bose condensate.

Such is the weird and wonderful quantum world. I must stop here, but you must travel on. Bon voyage!

---

**Exercise 18.2. Degenerate Bose Gas in 2D.** (a) Show that Bose condensation does not occur in 2D. *Hint.* The integral that you will get when you write the formula for $N$ is doable in elementary functions. You should find that $N \propto \ln(1 - e^{\beta\mu})$.

(b) Calculate the chemical potential as a function of $n$ and $T$ in the limit of small $T$. Sketch $\mu(T)$ from small to large $T$.

(c) Show that the heat capacity (at constant area) is $C \propto T$ at low temperatures and sketch $C(T)$ from small to large $T$.

**Exercise 18.3. Paramagnetism of Degenerate Bose Gas.** Consider a gas of bosons with spin 1 in a weak magnetic field, with energy levels

$$\varepsilon(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2m} - 2\mu_B s_z B, \quad s_z = -1, 0, 1, \tag{18.18}$$

where $\mu_B = e\hbar/2m_e c$ is the Bohr magneton.

(a) Derive an expression for the magnetic susceptibility of this system. Show that Curie's law ($\chi \propto 1/T$) is recovered in the classical limit.

(b) What happens to $\chi(T)$ as the temperature tends to the critical Bose-Einstein condensation temperature from above ($T \to T_c + 0$)? Sketch $\chi(T)$.

(c) At $T < T_c$ and for a given $B$, which quantum state will be macroscopically occupied? Taking $B \to +0$ (i.e., infinitesimally small), calculate the spontaneous magnetisation of the system,

$$M_0(n, T) = \lim_{B \to 0} M(n, T, B), \tag{18.19}$$

as a function of $n$ and $T$. Explain why the magnetisation is non-zero even though $B$ is vanishingly small. Does the result of (b) make sense in view of what you have found?

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## 19. Thermal Radiation (Photon Gas)

[Literature: Landau & Lifshitz (1980), §63]

*This part of the course was taught, in succession, by Professors Andrew Boothroyd, Julien Devriendt (2021), and Andrew Steane.*

**Exercise 19.1.** Work out the theory of thermal radiation using the results of Exercise 16.6.

**Exercise 19.2. Heat Capacity of Metals.** The objective here is to find at what temperature the heat capacity of the electron gas in a metal dominates over the heat capacity associated with the vibrations of the crystal lattice.

(a) Calculate the heat capacity of electrons in aluminium as a function of temperature for $T \ll T_{\rm F}$.

(b) To estimate the heat capacity due to the vibrations of the lattice, you will need to use the so-called *Debye model*. Derive it from the results you obtained in Exercise 16.6 as follows.

The vibrations of the lattice can be modelled as sound waves propagating through the metal. These in turn can be thought of as massless particles (*"phonons"*) with energies $\varepsilon = \hbar\omega$ and frequencies $\omega = c_{\rm s}k$, where $c_{\rm s}$ is the speed of sound in a given metal and $k$ is the wave number (a discrete set of allowed wave numbers is determined by the size of the system, as usual). Thus, the statistical mechanics for the phonons is the same as for photons, with two exceptions: (i) they have 3 possible polarisations in 3D (1 longitudinal, 2 transverse) and (ii) the wave number cannot be larger, roughly, than the inverse spacing of the atoms in the lattice (do you see why this makes sense?).

Given these assumptions,

— derive an expression for the density of states $g(\varepsilon)$ [or $g(\omega)$];

— derive an expression for the mean energy of a slab of metal of volume $V$;

— figure out the condition on temperature $T$ that has to be satisfied in order for it to be possible to consider the maximum wave number effectively infinite;

— calculate the heat capacity in this limit as a function of $T$; you may need to use the fact that $\int_0^\infty {\rm d}x\, x^3/(e^x - 1) = \pi^4/15$.

*Hint.* You already did all the required maths in Exercise 16.6, so all you need is to figure out how to modify it to describe the phonon gas. You will find it convenient to define the *Debye temperature*

$$\Theta_{\rm D} = \frac{\hbar c_{\rm s}(6\pi^2 n)^{1/3}}{k_{\rm B}}, \tag{19.1}$$

where $n$ is the number density of the metal. This is the temperature associated with the maximal wave number in the lattice, which Debye defined by stipulating that the total number of possible phonon modes was equal to 3 times the number of atoms:

$$\int_0^{k_{\max}} {\rm d}k\, g(k) = 3N. \tag{19.2}$$

For Al, $\Theta_{\rm D} = 394$ K.

(c) Roughly at what temperature does the heat capacity of the electrons in aluminium become comparable to that of the lattice? Al has valence 3 and density $n = 2.7\ {\rm g\,cm^{-3}}$. The speed of sound in Al is $c_{\rm s} \approx 6000$ m/s.

# PART VII
# Thermodynamics of Real Gases

[Literature: Landau & Lifshitz (1980), Ch. VII and VIII]

*This part of the course was taught, in succession, by Professors Andrew Boothroyd, Julien Devriendt (2021), and Andrew Steane.*

IUCUNDI ACTI LABORES.

## Acknowledgments

I am grateful to many at Oxford who have over the last five years given advice, commented, pointed out errors, asked challenging questions and generally helped me get a grip. A partial list is: tutors Michael Barnes, James Binney (who convinced me to handle entropy in the way I do and on whose unpublished lecture notes on Statistical Mechanics I have drawn in some of my own lectures), Steve Blundell, Andrew Boothroyd, Archie Bott, Radu Coldea, Julien Devriendt, Hadleigh Frost, John Gregg, Dieter Jaksch, Nick Jelley, Minhyong Kim, Adrian Menssen, Federico Nova, Sid Parameswaran, Armin Reichold, Steve Simon, Andrew Steane, students Tejas Acharya, Toby Adkins (who produced a set of rival course notes to explain to fellow students what I was really talking about), Laila Ahmed, Bruno Balthazar, Tim Chan, Matthew Elliot, Robert Ewart, Marco Fabus, Thomas Foster, Om Gupta, Tony He, Julian Huddart, Matias Janvin, Jakob Kastelic, Carolin Kohl, Krystof Kolar, Ziyan Li, Harry Plumley, Yungsong Tao, Leander Thiele, Guillermo Valle, Marjolein van der Linden, Yihan (Henry) Xu (as well as many others who asked good questions but never introduced themselves) and especially the many generations of Merton College 2nd-year undergraduates who had to endure not just my lecturing but also my tutoring—and in responding vigorously to the latter helped improve (I hope) the former.

## REFERENCES

Barenblatt, G. I. 1996 *Scaling, Self-similarity, and Intermediate Asymptotics*. Cambridge University Press.

Barenblatt, G. I. 2003 *Scaling*. Cambridge University Press.

Bekenstein, J. D. 1973 Black holes and entropy. *Physical Review D* **7**, 2333.

Berezin, F. A. 2007 *Lectures on Statistical Physics*. Moscow: MCCME Publishing.

Binney, J. & Skinner, D. 2013 *The Physics of Quantum Mechanics*. Oxford University Press.

Blundell, S. J. & Blundell, K. M. 2009 *Concepts in Thermal Physics*. Oxford University Press, 2$^{\text{nd}}$ Edition.

Boltzmann, L. 1995 *Lectures on Gas Theory*. Dover.

Bradbury, R. 1952 *A Sound of Thunder*. Collier.

Chandrasekhar, S. 2003 *Hydrodynamic and Hydromagnetic Stability*. Dover.

Chapman, S. & Cowling, T. G. 1991 *The Mathematical Theory of Non-uniform Gases*. Cambridge University Press, 3$^{\text{rd}}$ Edition.

Dellar, P. J. 2015 *Kinetic Theory of Gases*. Lecture Notes for the Oxford MMathPhys course on Kinetic Theory; URL: http://people.maths.ox.ac.uk/dellar/MMPkinetic.html.

Devriendt, J. 2021 *Lectures Notes on Thermodynamics and Statistical Mechanics*. Lecture Notes for the Oxford A1 Course; URL: https://www.physics.ox.ac.uk/system/files/file_attachments/all_thermo_notes.pdf.

Dunkel, J. & Hilbert, S. 2014 Consistent thermostatistics forbids negative absolute temperatures. *Nature Physics* **10**, 67.

Essler, F. H. L. 2009 *Mathematical Methods*. Lecture Notes for the Oxford Physics course; URL: http://www-thphys.physics.ox.ac.uk/people/FabianEssler/MathsMethods.html.

Ford, I. 2013 *Statistical Physics. An Entropic Approach*. Wiley.

Gibbs, J. W. 1902 *Elementary Principles in Statistical Mechanics Developed with Especial Reference to the Rational Foundation of Thermodynamics*. New York: Charles Scribner's Sons.

Ginzburg, V. L., Levin, L. M., Sivukhin, D. V. & Yakovlev, I. A. 2006 *Problems for a Course of General Physics II. Thermodynamics and Molecular Physics*. Moscow: Fizmatlit.

Gour, G. 1999 Schwarzschild black hole as a grand canonical ensemble. *Physical Review D* **61**, 021501(R).

Jaynes, E. T. 1965 Gibbs vs. Boltzmann entropies. *American Journal of Physics* **33**, 391.

Jaynes, E. T. 2003 *Probability Theory: The Logic of Science*. Cambridge: Cambridge University Press.

Kapitsa, P. L. 1974 *Experiment, Theory, Practice*. Moscow: Nauka.

Kardar, M. 2007 *Statistical Physics of Particles*. Cambridge: Cambridge University Press (online version—his MIT lecture course: https://ocw.mit.edu/courses/physics/8-333-statistical-mechanics-i-statistical-mechanics-of-particles-fall-2013/).

Landau, L. D. & Lifshitz, E. M. 1980 *Statistical Physics, Part 1 (L. D. Landau and E. M. Lifshitz's Course of Theoretical Physics, Volume 5)*. Pergamon Press.

Landau, L. D. & Lifshitz, E. M. 1981 *Quantum Mechanics: Non-Relativistic Teeory (L. D. Landau and E. M. Lifshitz's Course of Theoretical Physics, Volume 3)*. Elsevier.

Lewis, M. B. & Siegert, A. J. F. 1956 Extension of the condensation theory of Yang and Lee to the pressure ensemble. *Physical Review* **101**, 1227.

Lifshitz, E. M. & Pitaevskii, L. P. 1980 *Statistical Physics, Part 2: Theory of the Condensed State (L. D. Landau and E. M. Lifshitz's Course of Theoretical Physics, Volume 9)*. Pergamon Press.

Lifshitz, E. M. & Pitaevskii, L. P. 1981 *Physical Kinetics (L. D. Landau and E. M. Lifshitz's Course of Theoretical Physics, Volume 10)*. Elsevier.

Lukas, A. 2019 *Mathematical Methods*. Lecture Notes for the Oxford Physics course; URL: http://www-thphys.physics.ox.ac.uk/people/AndreLukas/MathMeth/.

Lynden-Bell, D. 1967 Statistical mechanics of violent relaxation in stellar systems. *Mon. Not. R. Astron. Soc.* **136**, 101.

Magorrian, J. 2017 *Mathematical Methods*. Lecture Notes for the Oxford Physics course; URL: http://www-thphys.physics.ox.ac.uk/people/JohnMagorrian/mm/.

Maxwell, J. C. 1860 Illustrations of the dynamical theory of gases.—Part I. On the motions and collisions of perfectly elastic spheres. *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science* **19**, 19.

Pauli, W. 2003 *Thermodynamics and the Kinetic Theory of Gases (Pauli Lectures on Physics, Volume 3)*. Dover.

Schekochihin, A. A. 2025 *Lectures on Kinetic Theory and Magnetohydrodynamics of Plasmas*. Lecture Notes for the Oxford MMathPhys programme; URL: http://www-thphys.physics.ox.ac.uk/people/AlexanderSchekochihin/KT/2015/KTLectureNotes.pdf.

Schrödinger, E. 1990 *Statistical Thermodynamics*. Dover.

Shannon, C. 1948 A mathematical theory of communication. *The Bell System Technical Journal* **27**, 379.

Sinai, Ya. G. 1992 *Probability Theory: An Introductory Course*. Springer.

Steane, A. M. 2017 *Thermodynamics. A complete undergraduate course*. Oxford University Press.

Szilard, L. 1929 On the decrease of entropy in a thermodynamic system by the intervention of intelligent beings. *Zeitschrift für Physik* **53**, 840, English translation in *Behavioral Science* **9**, 301 (1964).

Tong, D. 2012 *Lectures on Statistical Physics*. Lecture Notes for the Cambridge Mathematics course; URL: http://www.damtp.cam.ac.uk/user/tong/statphys.html.

Verlinde, E. 2011 On the origin of gravity and the laws of Newton. *Journal of High Energy Physics* **4**, 029.