

Lectures on Statistical Physics (AI)

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PART I. BASIC THERMODYNAMICS - taught by A. Boothroyd

PART II. KINETIC THEORY

S1. Statistical description of a gas.

1.1 Introduction

We have so far encountered two basic types of physics:

1) physics of single objects (or groups of just a few such objects). For classical (macroscopic) objects, we had a completely deterministic description based on Newton's 2nd law: given initial positions and velocities of all participating objects, ~~and the forces acting on them~~ 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 QM - where, however, again we typically deal with single (or not very numerous) objects and can solve differential equations that determine, eventually, probabilities of quantum states (generalising the mechanical notions of momentum, energy, angular momentum etc.)

2) physics of "systems" - understood to be large collections of objects (e.g. gas = \sum particles). This was introduced in Part I - and the description seemed to be

conducted in completely different terms, the key notions being internal energy, heat, temperature, entropy, volume, pressure etc. All these things were introduced largely without reference to the microscopic composition of the systems considered.

⇒ It is clear, however, 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 purposes of practical calculation: for example, while the relationship between energy, heat, pressure and volume could be established and then temperature introduced w/o specifying what the system under consideration was made of, we had, ~~however~~ in order to make practical quantitative predictions, to rely on experimentally determined empirical relations between

p, V and T (equation of state)

internal energy $\rightarrow U, V$ and T (usually via heat capacity) etc.

Statistical Mechanics (which we will study in HT) will deal with the ~~the~~ question of how, given some basic microphysical information about the properties of the system and some very general principles that a system in equilibrium must respect, we can derive the thermodynamics of the system (including, typically, $U(V, T)$, equ. of state, entropy $S(V, T)$, heat capacities etc.).

Kinetic Theory (which ^{we} will study for the simplest case of a classical monatomic ideal gas) is concerned not just with the properties of an equilibrium but with how the equilibrium is reached and so how the collective properties of a system evolve with time. This will require both a workable 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 SM. We study KT first perhaps because it is somewhat less abstract and more intuitive than SM. (as will recover the equilibrium results in SM)

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

Let's consider the simplest case: a classical gas, simplest model: ^{particles are} hard spheres, elastic collisions, forget QM.

Say we know all their positions and velocities at some $t=0$ (in fact, impossible even in principle, but we are ignoring QM)

Solve $m\ddot{\vec{r}} = \vec{F}$ for each. Problem solved?

Two difficulties arise:

1) Too much information

typical system $\sim 10^{23}$ particles (Ex.: estimate!)

So 1 data dump (\vec{r}, \vec{v} for each particle at one time)

takes about $\sim 10^{12}$ Tb

cf. all of Internet/yr $\sim 10^{10}$ Tb) so ~ 100 yrs of internet

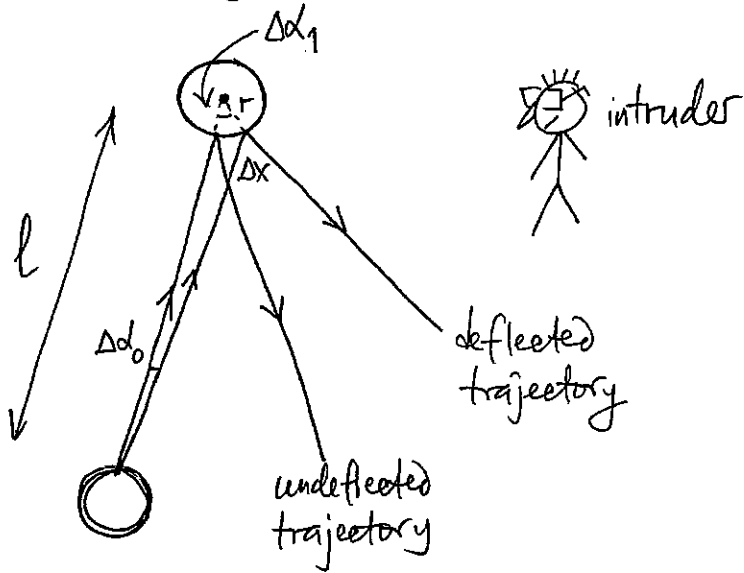
We can't process this.

2) Sensitivity to initial conditions and tiny perturbations.

Even if we could process these gazillions of particles, tiny errors would quickly change the story as any error in the initial conditions grows exponentially fast.

Example. Imagine we have a set of billiard balls on a table (frictionless), we set them in motion and want to observe them as time goes on. We could, in principle, solve their equations of motions and predict where they will all be ^{and} how fast they will be moving at any time $t > 0$ ($t=0$ is the time at which the initial conditions are given). It turns out that if someone enters the room during this experiment, the ~~de~~ small deflections of the balls due to his/her gravitational pull will accumulate to alter the trajectories completely after only ~ 10 collisions!

In case you think this is incredible, let me prove this.



For simplicity, let's consider all the balls fixed in space, one moving and colliding with them.



Distance between balls $\sim l \sim 30 \text{ cm}$

Size of the room $\sim L \sim 5 \text{ m}$

mass of intruder $\sim 80 \text{ kg}$

Deflection due to gravity $\Delta x \sim \frac{MG}{L^2} t^2 \sim 10^{-8} \text{ cm}$

Initial angular deflection

\uparrow time between collisions $\sim 1 \text{ sec}$

$$\Delta\alpha_0 \sim \frac{\Delta x}{l} \lll 1$$

Angular deflection after one collision:

$$\Delta\alpha_1 \sim \frac{\Delta x}{r} \sim \Delta\alpha_0 \left(\frac{l}{r} \right) \leftarrow \begin{array}{l} \text{factor by which angular} \\ \text{deflection is amplified} \\ \text{in one collision} \end{array}$$

\uparrow radius of ball $\sim 3 \text{ cm}$

After n collisions:

$$\Delta\alpha_n \sim \Delta\alpha_0 \left(\frac{l}{r} \right)^n \sim \frac{\Delta x}{l} \left(\frac{l}{r} \right)^n \sim 1$$

\leftarrow in order for trajectory to be changed significantly

So trajectory changed after

$$n \sim \frac{\ln(l/\Delta x)}{\ln(l/r)} \sim \frac{\ln 3 \cdot 10^9}{\ln 10} \sim 10 \text{ q.e.d.}$$

The basic idea is that if errors grow exponentially with the # of collisions, you don't need very many collisions to amplify to order 1 even very tiny initial perturbations ("butterfly effect")

A molecule of air at 1 atm at room temperature has $\sim 10^9$ collisions per second (we'll derive this later).

Thus molecule motion becomes essentially random (chaotic, deterministically unpredictable even for a classical system). So deterministic description is useless.

⇒ This is fine because we really are only interested in bulk properties of our system, not the motion of individual particles [we will learn later that in fact talking about the behavior of individual particles in a gas is often meaningless because particles can be indistinguishable].

{ If we can relate those bulk properties to averages over particle motion, we will determine everything we wish to know.

Let me explain how this is done.

1.2 Energy

So we model our gas as a collection of moving point particles, whose positions \vec{r} and velocities \vec{v} are random variables. [Let us consider a volume of such gas ~~with~~ with no spatial inhomogeneities, so all positions \vec{r} are equiprobable.]

The mean energy of N particles ~~is~~ comprising this system is

$\langle E \rangle = N \langle \frac{mv^2}{2} \rangle$ ← mean energy of 1 particle (1)

(assume all particles have the same distribution of velocities)

Note that in general, particles may have a mean velocity, i.e. the whole system may be moving at a velocity ~~in some direction~~ in some direction:

$\langle \vec{v} \rangle = \vec{u}$ by def.!

Let $\vec{v} = \vec{u} + \vec{w}$ ← peculiar velocity, $\langle \vec{w} \rangle = 0$. Then

$\langle E \rangle = N \frac{m}{2} \langle |\vec{u} + \vec{w}|^2 \rangle = \frac{Nm u^2}{2} + N \langle \frac{mw^2}{2} \rangle$ (2)

↑ assume they all have the same mass " $\frac{Nm u^2}{2} = K$ " kinetic energy of the system as a whole
" $\langle \frac{mw^2}{2} \rangle = U$ " internal energy

U is what figures in thermodynamics ("heat")
- mean energy of the disordered motion
("invisible motion" - they said in the 19th century)

if system is homogeneous, $\vec{u} = \text{const}$, so can just go to a frame moving with \vec{u}

For now, we'll assume $\vec{u} = 0$ as so

$$U = N \left\langle \frac{mV^2}{2} \right\rangle$$

1.3 Thermodynamic Limit

(3)

But is average energy really enough for a good description of a system? ~~energy fluctuation~~
~~energy fluctuation~~ How is this average energy related to the exact energy of our system? Here we are greatly helped by what we previously thought was a problem — the very large N .

It turns out that for $N \gg \gg 1$, the typical difference between average energy and exact energy is very small (and the same is true for other relevant quantities). Estimate it:

Exact energy $E = \sum_i \frac{mv_i^2$, $U = \langle E \rangle$

↑
velocity of particle i
Sum over particles, indexed by i

Then mean square fluctuation is

$$\langle (E-U)^2 \rangle = \langle E^2 \rangle - U^2 = \sum_{i \neq j} \left\langle \frac{mv_i^2}{2} \frac{mv_j^2}{2} \right\rangle - \left(\sum_i \left\langle \frac{mv_i^2}{2} \right\rangle \right)^2$$

assume, as before, that all particles have the same velocity distribution

$$= N \left\langle \frac{m^2 v^4}{4} \right\rangle + N(N-1) \left\langle \frac{mv^2}{2} \right\rangle^2 - N^2 \left\langle \frac{mv^2}{2} \right\rangle^2$$

particles are independent
 \uparrow
 $N^3 \begin{matrix} \nabla & \nabla & \nabla \\ 0 & 0 & 0 \end{matrix}$

$$= N \frac{m^2}{4} (\langle v^4 \rangle - \langle v^2 \rangle^2)$$

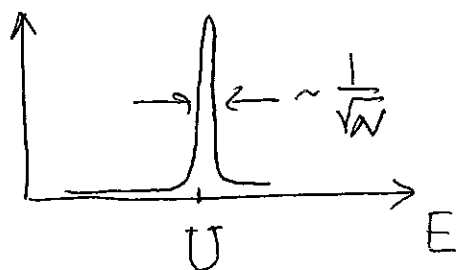
Thus, the relative mean square fluctuation is

$$\frac{\langle (E-U)^2 \rangle^{1/2}}{U} = \frac{\sqrt{N \frac{m^2}{4} (\langle v^4 \rangle - \langle v^2 \rangle^2)}}{N \langle \frac{mv^2}{2} \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{\langle v^4 \rangle}{\langle v^2 \rangle^2} - 1} \quad (4)$$

This is very small
for $N \gg \gg 1$

↑
this is clearly
independent
of N
(particle
property)

Thus, distribution of E around $U = \langle E \rangle$
is very sharply peaked.



This is called the
"thermodynamic limit"

(NB: This may break down if there are strong correlations between particles, i.e., $\langle v_i^2 v_j^2 \rangle \neq \langle v_i^2 \rangle \langle v_j^2 \rangle$ - fluctuations in such systems ~~are~~ ^{can be} very strong)

OK, I hope to have convinced you that averages
do tell us something about the system that is in some
sense a good representation of its actual state,
at least when the # of constituent particles is large.

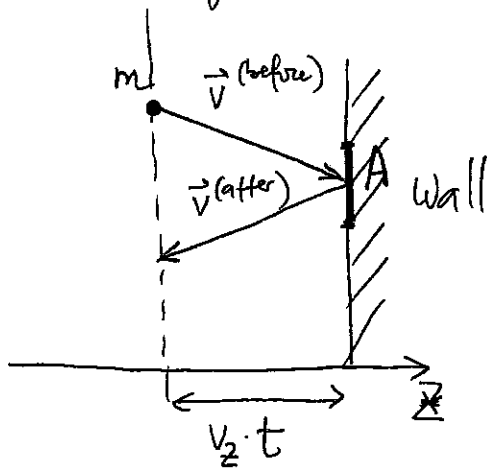
1.4 Kinetic Calculation of Pressure [see, e.g., Pauli §24]

The goal now is to work out how a bulk property of a volume of gas — pressure felt by the walls of a container (or by a body immersed in the gas) — is related to average properties of the moving particles.

Pressure = force per unit area

Force = momentum per unit time

Particles hit a surface (wall), bounce off (assume they do it elastically) — so pressure on the wall is momentum delivered to the wall per unit time per unit area ("momentum flux")



only particles from this interval will hit wall in time t

- When a particle bounces off a wall ~~elastically~~

$$v_x^{(after)} = -v_x^{(before)}$$

where \hat{x} is the direction \perp to the wall

and other components of velocity are unchanged.

- So, momentum delivered by the particle is

$$2m v_x$$

- Consider particles with \hat{x} -component of their velocity in the interval $[v_x, v_x + dv_x]$ (small dv_x)

Then the contribution of these particles to pressure is

$$dp(v_z) = 2mv_z \underbrace{d\Phi(v_z)}_{\substack{\uparrow \\ \text{\# of particles with } [v_z, v_z + dv_z] \\ \text{hitting the wall per unit time} \\ \text{per unit area}}} \quad (5)$$

particle flux

Consider wall area A and time t . Then

$$d\Phi(v_z) = \frac{dN(v_z)}{At} \leftarrow \substack{\text{\# of particles that hit} \\ \text{area } A \text{ over time } t} \quad (6)$$

$$dN(v_z) = \underbrace{A \cdot v_z t}_{\substack{\text{volume where a particle} \\ \text{must be to hit the} \\ \text{wall over time } t}} \cdot \underbrace{n}_{\substack{\text{\# density of particles} \\ \left(n = \frac{N}{V} \right)}} \cdot \underbrace{f(v_z) dv_z}_{\substack{\uparrow \\ \text{fraction of particles} \\ \text{with velocities in} \\ [v_z, v_z + dv_z]}} \quad (7)$$

Thus, 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 velocity distribution for a single particle (and we assume that all particles have the same pdf of their velocities)

Connection to probability theory :

$$f(v_z) dv_z = \text{probability for particle to have velocity in the interval } [v_z, v_z + dv_z]$$

$+\infty$

$$\int_{-\infty}^{+\infty} f(v_z) dv_z = 1 \quad \text{normalisation (total probability)}$$

$-\infty$

OK, let's collect everything together:

$$\boxed{d\Phi(v_z) = n v_z f(v_z) dv_z} \quad \left(\begin{array}{l} \text{flux of particles} \\ \text{with } [v_z, v_z + dv_z] \end{array} \right) \quad (8)$$

Therefore

$$dp(v_z) = 2m v_z d\Phi(v_z) = 2mn v_z^2 f(v_z) dv_z \quad (9)$$

To get total pressure we integrate this over all particles with $v_z > 0$ (those that are moving towards the wall)

$$p = \int_0^{\infty} 2mn v_z^2 f(v_z) dv_z \quad (10)$$

Assume $f(-v_z) = f(v_z)$, i.e. no preference for motion in any particular direction (e.g. wall is not attractive!)

Then

$$p = mn \int_{-\infty}^{+\infty} v_z^2 f(v_z) dv_z = mn \langle v_z^2 \rangle \quad \begin{array}{l} \text{(11)} \\ \text{mean square} \\ \text{velocity in} \\ \text{z direction} \end{array}$$

This was a 1D calculation, but in fact it is quite general. In 3D, the distribution of particle velocities is described by

$$\underbrace{f(v_x, v_y, v_z) dv_x dv_y dv_z}_{\text{|| } f(\vec{v}) \text{ pdf in 3D}} = \underbrace{\text{probability for particle velocity to be in the "cube" } \vec{v} \in [v_x, v_x + dv_x] \times [v_y, v_y + dv_y] \times [v_z, v_z + dv_z]}_{\text{this is a joint probability for the three random variables } v_x, v_y, v_z}$$

The 1D pdf is simply

$$f(v_z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(v_x, v_y, v_z) dv_x dv_y$$

So, I can write

$$p = mn \int d^3\vec{v} v_z^2 f(\vec{v}) = mn \langle v_z^2 \rangle \quad (12)$$

(where z , by definition, is the direction perpendicular to the wall on which we are calculating the pressure)

1.5 Isotropic Distributions

Let us now make a further assumption: all directions are statistically the same (isotropy). Then

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

because $v^2 = v_x^2 + v_y^2 + v_z^2$

$$\text{So, } p = \frac{1}{3} mn \langle v^2 \rangle = \frac{2}{3} \frac{U}{V} \quad \left(\begin{array}{l} \text{total energy, as calculated} \\ \text{on pp. 7-8} \\ \text{energy density} \\ \text{volume} \end{array} \right) \quad (13)$$

- pressure is simply $\frac{2}{3}$ of mean internal energy per unit volume! (makes sense: p is to do with how vigorously particles bombard the wall) ended here

For future use, let us see what isotropy means for the pdf: obviously, it must be independent of the direction of \vec{v} , so $f(\vec{v}) = f(v)$

\uparrow f is of speed alone

For such systems, it is convenient to change variables: $(v_x, v_y, v_z) \rightarrow (v, \theta, \phi)$ polars in \vec{v} space

$$f(\vec{v}) dv_x dv_y dv_z = f(\vec{v}) \left| \frac{\partial(v_x, v_y, v_z)}{\partial(v, \theta, \phi)} \right| dv d\theta d\phi$$

joint pdf of v_x, v_y, v_z

joint pdf of v, θ, ϕ

$v^2 \sin \theta$ Jacobian

(This is a general rule for how pdfs transform when variables are changed)

So, joint pdf of v, θ, φ is

$$\tilde{f}(v, \theta, \varphi) = f(\vec{v}) v^2 \sin \theta \quad (14)$$

Pdf of speeds:

$$\begin{aligned} \tilde{f}(v) &= \int_0^\pi d\theta \int_0^{2\pi} d\varphi \tilde{f}(v, \theta, \varphi) = f(v) \text{ if isotropic} \\ &= \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta v^2 \overbrace{f(\vec{v})} = 4\pi v^2 f(v) \end{aligned} \quad (15)$$

[NB: Blundell calls the distr. of speeds f and the distr. of velocities g , so my f is B's g and my \tilde{f} is B's f]

To make sure everything is consistent, let us calculate again

$$\begin{aligned} p &= mn \langle v_z^2 \rangle = mn \int d^3 \vec{v} v_z^2 f(\vec{v}) = \text{isotropic} \\ &= mn \int_0^\infty dv \int_0^\pi d\theta \int_0^{2\pi} d\varphi v^2 \sin \theta \underbrace{v^2 \cos^2 \theta}_{\substack{= \\ \frac{2}{3}}} f(v) = \\ &= mn \int_0^\infty dv v^4 f(v) \cdot 2\pi \cdot \int_0^\pi d\cos \theta \cos^2 \theta = \\ &= \frac{4\pi}{3} mn \int_0^\infty dv v^4 f(v) = \frac{1}{3} mn \int_0^\infty dv v^2 \tilde{f}(v) = \frac{1}{3} mn \langle v^2 \rangle \end{aligned}$$

Exercise. Prove $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \frac{1}{3} mn \langle v^2 \rangle$

Calculate $\langle v_x v_y \rangle, \langle v_x v_z \rangle, \langle v_y v_z \rangle$

(could you have guessed the result from symmetry arguments?)

q.e.d.