

§10. Statistical Mechanics of Classical Ideal Gas.

So let us see now if we can actually fulfill the stat. mech. programme outlined above for the system that we studied as a team in ~~the~~ Part I of this course - we know what the answers must be, so let's see if we can recover them within this more general framework we have constructed.

All we need to calculate is the partition function

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$$

where E_{α} is energy of our system (gas in a box) and α all possible states in which it can collectively find itself. But what ^{we} in fact know are the energies that a single particle can have in a microstate determined by its momentum \vec{p} . In the non-relativistic limit, the particle's energies are

$$E_{\vec{p}} = \frac{p^2}{2m} \quad (\text{please do not confuse momentum with pressure } P \text{ or probability } p \text{!})$$

The system's total energies E_{α} are sums of energies $E_{\vec{p}}$ of individual particles and naively, we might think that the microstates ~~are~~ of the system are described by a list of momenta of all particles: $\alpha = \{\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N\}$, $N = \#$ of particles.

This approach will turn out to be very wrong indeed, but let us explore what its implications are — we will learn certain useful things and will also be able to fix it later without redoing much of the work.

10.1 One-particle Partition Function

As we argued before, if we can subdivide the system into parts and energy levels of these parts are independent, then the energy levels of the combined system are sums of those of the parts and the partition functions multiply (p.64):

$$Z = \sum_{\{\vec{p}_1 \dots \vec{p}_N\}} e^{-\beta(\epsilon_{\vec{p}_1} + \dots + \epsilon_{\vec{p}_N})} = \left[\sum_{\vec{p}} e^{-\beta \epsilon_{\vec{p}}} \right]^N = Z_1^N$$

Let us calculate Z_1 .

Z_1 "one-particle partition function"

We have a technical issue:

we are used to thinking of momenta as continuous, but here we have a discrete sum.

Well, actually, in QM, a particle with a definite momentum \vec{p} is in fact a monochromatic wave with wave number $\vec{k} = \frac{\vec{p}}{\hbar}$ and if it lives in a box, $L_x \times L_y \times L_z$ (Planck const)

~~these~~ these wave numbers quantize so an integer # of periods can fit in the box: integers,

$$\vec{k} = \left(\frac{2\pi}{L_x} n_x, \frac{2\pi}{L_y} n_y, \frac{2\pi}{L_z} n_z \right)$$

Thus, $\sum_{\vec{p}} = \sum_{\vec{k}}$ is indeed discrete. However, it can be approximated by an integral if we can have

$$k_x \gg \Delta k_x = \frac{2\pi}{L_x} \quad \text{and similarly for } y, z.$$

Clearly, this is possible unless the temperature is very low, i.e. if

$$k_B T \gg \frac{\hbar^2 \Delta k^2}{2m} \sim \frac{\hbar^2 (2\pi)^2}{2mL^2} \sim \frac{\hbar^2}{mV^{2/3}}$$

(~~degeneracy is not a problem~~)

$$\begin{aligned} \text{Then } z_1 &= \sum_{\vec{p}} e^{-\beta \epsilon_{\vec{p}}} = \sum_{\vec{k}} \frac{L_x L_y L_z}{(2\pi)^3} \Delta k_x \Delta k_y \Delta k_z e^{-\beta \frac{\hbar^2 k^2}{2m}} \\ &\approx \frac{V}{(2\pi)^3} \int d^3 \vec{k} e^{-\beta \frac{\hbar^2 k^2}{2m}} = \\ &= \frac{V}{(2\pi)^3} 4\pi \int_0^\infty dk k^2 e^{-\beta \frac{\hbar^2 k^2}{2m}} \end{aligned}$$

↑ isotropic in \vec{k}

It is conventional to refer to this prefactor as density of states: $g(k) = \frac{V k^2}{2\pi^2}$. This underscores

the fact that energy levels are degenerate — there are many microstates (many \vec{p} , or \vec{k}) with the same energy and $g(k)$ tells us how densely their clutter per k : $g(k) dk$ is the # of states in a spherical shell.

{ Note: you get the same $g(k)$ if you assume the box periodic }
 { or if particles are standing waves confined in the box. }

$$\text{Thus, } Z_1 = \int_0^\infty dk g(k) e^{-\beta \hbar^2 k^2 / 2m}$$

It was nice to write it like this, but the integral is in fact easier to do so:

$$\begin{aligned} Z_1 &= \frac{V}{(2\pi)^3} \int d^3k e^{-\beta \hbar^2 k^2 / 2m} = \frac{V}{(2\pi)^3} \left[\int dk_x e^{-\beta \hbar^2 k_x^2 / 2m} \right]^3 \\ &= \frac{V}{(2\pi)^3} \pi^{3/2} \left(\frac{2m}{\beta \hbar^2} \right)^{3/2} = V \frac{1}{\hbar^3} \left(\frac{mk_B T}{2\pi} \right)^{3/2} \equiv \frac{V}{\lambda_{th}^3} \end{aligned}$$

where $\lambda_{th} = \hbar \sqrt{\frac{2\pi}{mk_B T}}$ is the "thermal wavelength"

This then tells us that the N -particle partition fn is

$$Z = Z_1^N = \left(\frac{V}{\lambda_{th}^3} \right)^N$$

and so $F = -k_B T \ln Z = -k_B T N \ln \frac{V}{\lambda_{th}^3}$ free energy

Are we done? Let's see: pressure:

$$\left[p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V} = n k_B T \text{ equ. of state of ideal gas } \checkmark \right]$$

entropy:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = k_B N \ln \left(\frac{V}{\lambda_{th}^3} \right)^{\frac{N}{n}} + \frac{3}{2} k_B N =$$

$$= k_B \left[N \ln N + \frac{3}{2} N - N \ln(n \lambda_{th}^3) \right]$$

(non-extensive)

But this is absolutely horrendous! It's not additive!

E.g., double the ~~amount of gas~~ amount of gas:

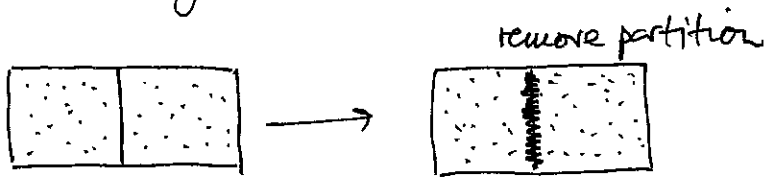
$$N \rightarrow 2N, V \rightarrow 2V (n = \text{const}) \Rightarrow S_{\text{new}} - 2S_{\text{old}} = k_B 2N \ln 2!$$

The offending term

10.2 Gibbs Paradox

This issue is best illustrated - and then resolved - by considering a famous example leading to the so-called Gibbs Paradox.

Mix two gases:



If the gases are different, we get

$$\Delta S = 2Nk_B \ln 2 \quad (\text{Ex. in homework})$$

But if they are the same, we get the same expression again ~~from our formula~~ from our formula for S of an ideal gas. We were not surprised to see entropy rise ~~as~~ as a result of mixing two different gases (clearly an irr. process, can't unmix them!) - but if the gases are the same, surely, we can reinsert the partition and end up with the same macrostate as originally?

10.3 Distinguishability

This gives us an idea what was wrong in our calculation of entropy (and it was wrong - whatever you think about mixing volumes of identical gas, a non-additive expression for entropy won't do, it completely undermines ~~our~~ ^{much} of our previous theory).

We counted the ~~states~~ states of the system in a way that distinguished between individual particles even if they had the same momentum \vec{p} .

So in the Gibbs set up we got ~~an apparent~~ ^{a spurious} entropy increase by moving ~~the~~ "individual" particles from one side of the box to another (in a sense, we were mixing N different gases, 1 particle of each!)

In QM, this problem does not in fact arise because particles are indistinguishable (interchanging them is just permutation argument of some big symmetric ~~function~~ wave function amplitude) - not just indistinguishable by us, but indistinguishable in principle (recall the uncertainty principle, we

} might say that distinguish particles is like saying "This one" or "that one", pointing at individual particles - but since their \vec{p} 's are definite, their positions are completely unspecified, they are just waves in a box!)

Thus, ~~the~~ the microstates are not

$$\alpha = \{ \vec{p}_1 \dots \vec{p}_N \} \quad (\text{momentum of each particle})$$

$$\text{but } \alpha = \{ n_1, n_2, n_3, \dots \}, \quad \sum_i n_i = N$$

where i indexes the (discrete) values that \vec{p} can have and n_i is the # of particles with ~~that~~ ^{i -th} value of \vec{p} ("occupation numbers").

$$\rightarrow i = \left(\frac{2\pi}{L_x} i_x, \frac{2\pi}{L_y} i_y, \frac{2\pi}{L_z} i_z \right)$$

Thus, the correct expression for the partition function is

Thus, the basic object is the whole box, not ind. particles!

$$Z = \sum_{\{n_1, n_2, \dots\}} e^{-\beta \sum_i n_i \epsilon_i}$$

\uparrow sets of occ. #'s - microstates
 \uparrow energy levels of the collective microstate
 \uparrow energy levels of single particle

In general, calculating this is quite a hard combinatorial problem (which we will solve in HT).

It is made easier if we are allowed to neglect all those microstates in which more than one particle occupies the same energy level. Then our old exp'n works except for the overcounting of the microstates in which particles are simply permuted - since they are indistinguishable, this should not be regarded as a different microstate. So

$$Z = \frac{Z_1^N}{N!}$$

of permutations

L. II ended here.

This is a good assumption as long as the # of available energy levels \gg # of particles.

Easy way to estimate this:

of quantum states $\sim \int_0^k dk g(k) \sim \frac{V}{\lambda_{th}^3} \gg N$ # of particles $\Rightarrow n \lambda_{th}^3 \ll 1$

$k \leftarrow$ typical $k \sim \sqrt{\frac{2mk_B T}{\hbar^2}} \sim \lambda_{th}^{-1}$
 (e.g. electrons in metal)

When this breaks down, we have to worry about "quantum correlations" - how many particles are allowed to share a state (HT!)

(cf. argument on p. 6a - same reasoning, basically)

Room temperature:
 $n \sim 10^{25} \text{ m}^{-3}$
 $n_Q \sim 10^{30} \text{ m}^{-3}$
 (for N_2)

$\text{or } n \ll n_Q = \lambda_{th}^{-3}$
 \uparrow quantum concentration

Note. The old formula, $Z = Z_1^N$, is not completely useless - it will apply to systems of distinguishable objects (e.g. spins in a lattice, where each is distinguished by where it sits).

10.4 Recover Results from Kinetics

So, the new improved partition function is

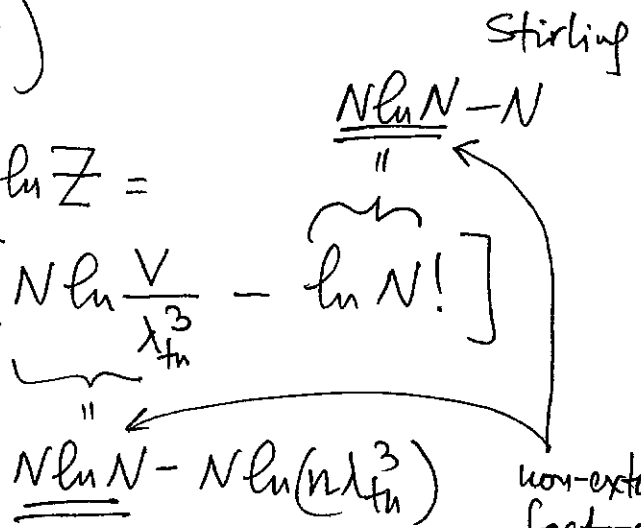
$$Z = \frac{1}{N!} \left(\frac{V}{\lambda_{th}^3} \right)^N$$

Free energy : $F = -k_B T \ln Z =$

$$= -k_B T \left[N \ln \frac{V}{\lambda_{th}^3} - \ln N! \right]$$

Thus,

$$F = -k_B T N \left[1 - \ln(n \lambda_{th}^3) \right]$$



Entropy

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = k_B N \left[\frac{5}{2} - \ln(n \lambda_{th}^3) \right]$$

nice and additive, Gibbs paradox no longer a paradox (check!) Sackur-Tetrode Equation

Now we can go ahead and check that our old results are recoverable from this.

Energy $U = F + TS = \frac{3}{2} k_B T N$

Recall that our old ^{kinetic} definition of temperature was

$$\frac{3}{2} k_B T = \left\langle \frac{mv^2}{2} \right\rangle \text{ mean energy per molecule}$$

So $T_{kinetic} = T_{stat. Mech.}$! (what energy is is unambiguous) of course

Pressure. $p = - \left(\frac{\partial F}{\partial V} \right)_T = + k_B T \frac{N}{V} = n k_B T$
equation of state.

So $P_{kinetic} = P_{stat. Mech.}$!

Note. The only thing the equation of state of the ideal gas depended on was $Z \propto V^N$ - thus issues of distinguishability and even precise structure of single-particle energy levels do not affect it [it will change if, for example, particles start crowding each other out of parts of volume - as indeed happens in "real" gases (HT!)]

Let's also calculate heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} k_B N$$

for the whole box.

- per particle $\frac{3}{2} k_B$

- per u. vol. $\frac{3}{2} k_B n$

- per u. mass $\frac{3}{2} k_B \rho$

cf. p. 32 (in heat diff. eqn)

You will soon learn that this only works for monatomic gases.
 Diatomic + hbd in a few lectures.

This concludes the Intro to SM. In what follows you will

with Prof. Boothroyd

- learn to operate thermodynamics practically (often using the eq. of state for ideal gas)
- learn to compute Z for many other systems (see p. 82)
- in HT, we'll solve the microstate-counting problem w/o ~~current~~ neglect of quantum correlation and discover some weird and wonderful quantum behaviours [we'll also show how classical ideal gas arises in the limit of low densities and high temperatures]
- in HT, more thermodynamics: real gases, phase transitions etc.