

## § 11. Statistical Mechanics of Classical Monatomic Ideal Gas

I am now going to show you your first example of a stat. mech. calculation that starts with energy levels for a system, then

- works out  $Z$  (and, therefore,  $F$ )
- calculates from that
  - the eqn of state
  - energy ( $\Rightarrow$  heat capacity)
  - entropy

We shall do this for a familiar system - classical monatomic ideal gas, for which we already know the answers (obtained from bespoke theory) and so can convince ourselves of the soundness of our new, much more general, formalism by recovering those answers.

We need 
$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}}, \quad (1)$$

where  $\{E_{\alpha}\}$  are energies of the system (gas in a box of volume  $V$ ) corresponding to all possible states  $\{\alpha\}$  in which it can collectively find itself.

Well, we do know what the <sup>possible</sup> ~~energy~~ states ~~of~~ and energies are for a single particle:

Its states are determined by its momentum  $\vec{p}$  and the corresponding energy is

$$\epsilon_{\vec{p}} = \frac{p^2}{2m} \quad (2) \quad \left[ \begin{array}{l} \text{please do not confuse} \\ \text{momentum } \vec{p} \text{ with pressure } P \\ \text{or probability } P_x! \end{array} \right]$$

Classically, we might be tempted to say that the states are determined also by positions  $\vec{r}$ , but we know from QM that we can't know both  $\vec{p}$  and  $\vec{r}$  exactly.

So we are considering  $\sqrt[3]{V}$  particle in a homogeneous box, the momentum is fixed and the particle can be anywhere — in fact, it is a monochromatic wave with wave #  $\vec{k} = \frac{\vec{p}}{\hbar}$  and if it lives in a box of dimensions  $L_x \times L_y \times L_z$ , the wave #'s quantize so an integer # of periods can fit in the box:

$$\vec{k} = \left( \frac{2\pi}{L_x} n_x, \frac{2\pi}{L_y} n_y, \frac{2\pi}{L_z} n_z \right) \quad (3)$$

↑ integers

$$\text{and } \epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \quad (4)$$

We have  $N$  such particles in the box.

The gas is ideal, so they are non-interacting and so you might think, naively, that this is a case of a composite system containing  $N$  subsystems each with known energy levels (4) and microstates (3).

If so, then the microstates of the collective would be

$$\Omega = \{ \vec{k}_1, \vec{k}_2, \dots, \vec{k}_N \} \quad (5)$$

with energies

$$E_\Omega = \sum_{i=1}^N \epsilon_{\vec{k}_i} \quad (6)$$

This approach 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.

10.2 Single-particle partition function

Under the above scheme, the partition function is

$$Z = \sum_{\{ \vec{k}_1, \dots, \vec{k}_N \}} e^{-\beta(\epsilon_{\vec{k}_1} + \dots + \epsilon_{\vec{k}_N})} = \left[ \sum_{\vec{k}} e^{-\beta \epsilon_{\vec{k}}} \right]^N = Z_1^N \quad (7)$$

(recall 10.1: partition functions of independent systems multiply)

$Z_1$  "single-particle partition fu"

So we calculate  $Z_1$ , approximating  $\sum$  with an integral:

$$Z_1 = \sum_{\vec{k}} e^{-\beta \epsilon_{\vec{k}}} = \sum_{\vec{k}} \underbrace{\frac{L_x L_y L_z}{(2\pi)^3}}_{=V \text{ volume}} \underbrace{\Delta k_x}_{\frac{2\pi}{L_x}} \underbrace{\Delta k_y}_{\frac{2\pi}{L_y}} \underbrace{\Delta k_z}_{\frac{2\pi}{L_z}} e^{-\beta \frac{\hbar^2 k^2}{2m}}$$

"grid size in k space"

$$\approx \frac{V}{(2\pi)^3} \int d^3 \vec{k} e^{-\beta \frac{\hbar^2 k^2}{2m}} \quad (8)$$

$k_B T \gg \frac{(2\pi)^2 \hbar^2}{2m V^{2/3}}$   
 $\uparrow$  good approximation as long as  $k \sim \frac{\sqrt{2mk_B T}}{\hbar} \gg \Delta k \sim \frac{2\pi}{V^{1/3}}$

This is actually the same as T >> Tdeg (see 2.3 Validity of Cl. Limit p. 22)

Easy to do the Gaussian integral:

$$Z_1 = \frac{V}{(2\pi)^3} \left[ \int dk_x e^{-\beta \hbar^2 k_x^2 / 2m} \right]^3 = \frac{V}{(2\pi)^3} \left[ \frac{2m}{\beta \hbar^2} \pi \right]^{3/2}$$

$$= V \frac{1}{\hbar^3} \left( \frac{mk_B T}{2\pi} \right)^{3/2} \equiv \frac{V}{\lambda_{th}^3}, \quad (9)$$

where  $\lambda_{th} = \frac{1}{\hbar} \sqrt{\frac{2\pi}{mk_B T}}$  is the "thermal wavelength"

### 11.3 Dispersion: Density of States

Since the integrand in (8) is isotropic in  $\vec{k}$ ,

$$Z_1 = \int_0^\infty dk \frac{V}{(2\pi)^3} \cdot 4\pi k^2 e^{-\beta \hbar^2 k^2 / 2m} \equiv \int_0^\infty dk g(k) e^{-\beta \epsilon(k)} \quad (10)$$

where  $g(k) = \frac{V k^2}{2\pi^2}$  is the "density of states" of a single particle — it measures how many states with the same energy there are per  $k$

$(g(k)dk = \# \text{ of states in a spherical shell in } k \text{ space}$   
 - so energy levels are increasingly more degenerate as  $k$  goes up.

Note that the level of this degeneracy depends on the dimension of space.)

**11.4 Disaster Strikes**

OK, let us ~~recover~~ recover our thread...

The  $N$ -particle partition function is (according to (71)):

$$Z = Z_1^N = \left( \frac{V}{\lambda_{th}^3} \right)^N \quad (11)$$

↑  
eq. (9)

Energy:  $U = - \frac{\partial \ln Z}{\partial \beta} = - \frac{\partial}{\partial \beta} \left[ N \ln \left( \frac{V}{h^3} \left( \frac{m}{2\pi\beta} \right)^{3/2} \right) \right]$

$$= N \cdot \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T N \quad \text{so far so good} \quad (12)$$

Free energy:  $F = -k_B T \ln Z = -k_B T N \ln \frac{V}{\lambda_{th}^3}$

Equ. of state:  $P = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V} = n k_B T \quad (13)$

Entropy:  $S = - \left( \frac{\partial F}{\partial T} \right)_V = k_B N \ln \left( \frac{V}{\lambda_{th}^3} \right) + k_B T N \frac{3}{2} \cdot \frac{1}{T} =$

all is still well

$$= k_B N \left[ \ln N + \frac{3}{2} - \ln(n \lambda_{th}^3) \right] \left( \frac{N}{n \lambda_{th}^3} \right) \quad (14)$$

This is terrible! It is not additive!!!

E.g. double the amount of gas:

$$N \rightarrow 2N, V \rightarrow 2V \quad (n = \text{const})$$

⇓

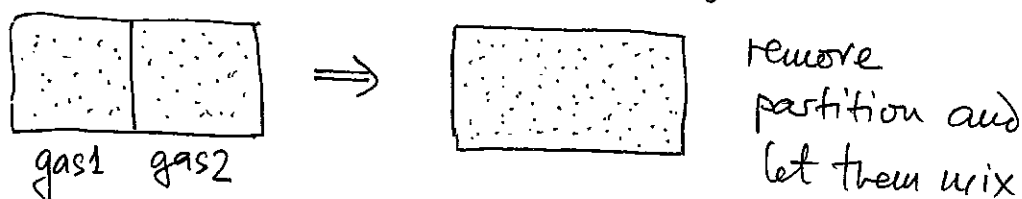
$$S_{\text{new}} - 2 S_{\text{old}} = 2 k_B N \ln 2 !$$

But (remember 10.1), we have built everything in such a way that  $S$  should be additive!

So what went wrong?

### 11.5 Gibbs Paradox

This issue is best illustrated - and then resolved -  
- by considering a famous example:



Each gas expands into vacuum, so each picks up  $Nk_B \ln 2$  of entropy and we get

$$\Delta S = 2Nk_B \ln 2 \quad (15)$$

- certainly if the two gases are different

[another way to see it is by ~~ε~~ arguing that after the partition is removed there is additional uncertainty as to whether each particle is on the left or on the right, so additional entropy

per particle is  $\Delta S_1 = -k_B \left( \frac{1}{2} \ln \frac{1}{2} \right) \cdot 2$ ,

So for  $2N$  particles, ↑  
2 possibilities:  $p_1 = p_2 = \frac{1}{2}$

$$\Delta S = 2N \cdot k_B \ln 2 ]$$

But if the gases are the same, surely the entropy must be the same - if we reinserted the partition, we would be back to the <sup>original</sup> ~~same~~ situation!

So then  $\Delta S = 0$ .

## 11.6 Distinguishability

This gives us an idea about where the problem came from: when we counted the states of the system, we distinguished between individual particles: e.g. swapping momenta between two particles corresponded to a different microstate in our accounting scheme.

So, in the Gibbs set up, we got a spurious entropy increase by moving "individual" particles from one side of the box to another (effectively, we are mixing  $N$  different gases, 1 particle of each)

In QM, this problem does not arise because particles are indistinguishable (interchanging them amounts to permuting arguments of some big symmetric wave function amplitude)

[One way of explaining this is by saying that distinguishing particles amounts to saying "this one" or "that one", pointing at their positions - but since their momenta are definite, their positions are completely unspecified, by uncertainty principle, they are just waves in a box!

In PART IV on applications, you'll see that in systems where individual ~~particles~~ particles can be viewed as distinguishable they are often fixed in some spatial positions, e.g. magnetizable spins in a lattice ]

Thus, the microstates for gas in a box are not

$$\alpha = \{ \vec{k}_1, \dots, \vec{k}_N \} \quad (\text{momenta of individual particles})$$

but in fact

$$\alpha = \{ n_1, n_2, n_3, \dots \}, \quad \sum n_i = N \quad (16)$$

where  $\{n_i\}$  are occupation numbers of microstates indexed by  $i = (\frac{2\pi}{L_x} i_x, \frac{2\pi}{L_y} i_y, \frac{2\pi}{L_z} i_z)$  - all possible discrete values that the wave# can take.

The corresponding energy levels (collective!) are

$$E_\alpha = \sum_i n_i \epsilon_i \quad (17)$$

↑ energy levels of a single particle

### 11.7 The Correct Partition Function

So, what we really must calculate is

$$Z = \sum_{\{n_1, n_2, \dots\}} e^{-\beta \sum_i n_i \epsilon_i} \quad (18)$$

↑ all possible sequences of occupation #'s (subject to  $\sum_i n_i = N$ )



In general, calculating this is ~~an~~ a tricky combinatorial problem - we will solve it in PART V, but for now we can use a shortcut.

Suppose we are allowed to neglect all those microstates in which more than one particle occupies the same energy level (i.e.  $n_i = 0$  or  $1$ ).

Then actually our old way of calculating  $Z$  is fine except for the overcounting of the microstates in which particles are simply permuted - since ~~they~~ <sup>particles</sup> are indistinguishable, these are not different microstates.

Compensating for that,

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

(19)

Note: The old formula  $Z = Z_1^N$  is still fine for systems of distinguishable objects.

How good is this assumption? We need

# of available energy levels  $\gg$  # of particles  $N$

$\int dk g(k) \sim \frac{V}{\lambda_{th}^3} \gg N \Leftrightarrow$

$$n \lambda_{th}^3 \ll 1 \quad (20)$$

Introduce  $n_Q = \frac{1}{\lambda_{th}^3}$  "quantum concentration",

we need

$$n \ll n_Q$$

This is actually the same condition as for classical limit,  $T \gg T_{deg.}$  (see p.22 and p.101)

E.g., at 1 atm and room temperature, for air,

$$n \sim 10^{25} \text{ m}^{-3} \quad \text{and} \quad n_Q \sim 10^{30} \text{ m}^{-3} \quad \text{OK!}$$

When (20) breaks down, we have a quantum gas — and must worry about "quantum correlation": how many identical particles are allowed to share the same microstate. We'll do this in PART V of the course.

11.8 Thermodynamics of ideal gas.

$$\text{So, } Z = \frac{1}{N!} \left( \frac{V}{\lambda_{th}^3} \right)^N, \quad \text{where } \lambda_{th} = \frac{1}{v} \sqrt{\frac{2\pi}{mk_B T}} \quad (21)$$

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

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

$\underbrace{\hspace{10em}}_{N \ln N - N} \quad \underbrace{\hspace{10em}}_{N \ln N - N}$

Stirling

$$= -k_B T N \left[ 1 - \ln(n \lambda_{th}^3) \right] \quad (22)$$

nonextensive bit happily cancels!

Entropy:  $S = - \left( \frac{\partial F}{\partial T} \right)_V =$

$$= + k_B N \left[ 1 - \ln(n \lambda_{th}^3) \right] + k_B T N \cdot \frac{3}{2} \frac{1}{T}$$

$$= k_B N \left[ \frac{5}{2} - \ln(n \lambda_{th}^3) \right] \quad (23)$$

Sackur-Tetrode Equation

Nice and additive, no Gibbs Paradox.

Energy :  $U = F + TS = \frac{3}{2} k_B T N$  (24)

Eq. of state :  $P = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T \frac{N}{V} = n k_B T$  (25)

Note : • The only thing that matters for the equation of state is  $Z \propto V^N$  - so neither distinguishability nor even the precise structure of energy levels ~~matters~~ affect the outcome [it will change when particles start crowding each other out of parts of the volume - as indeed happens in "real" gases - see PART VI]

Heat capacity :  $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} k_B N$  (26)

Note : • This works for monatomic gases.

In PART IV, on applications, you'll learn how to handle diatomic gases, where molecules can have energy levels due to rotational and vibrational degrees of freedom.

Finally, note that eqs. (24) and (25) constitute proof that

defined p. 20	$T_{\text{kinetic}} = T_{\text{stat. Mech}}$ $P_{\text{kinetic}} = P_{\text{stat. Mech}}$	defined as $1/k_B \beta$ in Gibbs distr. defined eq. (8) p. 68
	defined eq. (12) p. 13	(27)

Thus, all is consistent, we <sup>have</sup> recovered the same thermodynamics from S.M. as from K.T.

What about Maxwell's distribution itself?

The distribution function as we defined it is directly related to mean occupation #.

Indeed,  $\langle n_{\vec{k}} \rangle =$  mean # of particles in the state set by  $\vec{k}$  (or  $i$ , as we called it to emphasize discreteness)

$f(\vec{v}) d^3\vec{v} =$  mean fraction of particles in states set by  $[\vec{v}, \vec{v} + d^3\vec{v}]$

Then

$$\begin{aligned} f(\vec{v}) d^3\vec{v} &= \langle n_{\vec{k}} \rangle \cdot \frac{V}{(2\pi)^3} d^3\vec{k} \cdot \frac{1}{N} = \\ &= \frac{\langle n_{\vec{k}} \rangle}{N} \frac{V}{(2\pi)^3} d^3\left(\frac{m\vec{v}}{\hbar}\right) = \frac{\langle n_{\vec{k}} \rangle}{n} \frac{m^3}{(2\pi\hbar)^3} d^3\vec{v} \end{aligned}$$

Thus,

$$\boxed{f(\vec{v}) = \left(\frac{m}{2\pi\hbar}\right)^3 \frac{\langle n_{\vec{k}} \rangle}{n}} \quad (28)$$

but we are not yet ready to calculate  $\langle n_{\vec{k}} \rangle$  from S.M. (we will do this soon) - the result will have to be

$$\langle n_{\vec{k}} \rangle = n \left(\frac{2\pi\hbar}{m}\right)^3 \frac{e^{-\overbrace{v^2/v_{th}^2} = \frac{mv^2}{2k_B T} = \beta \frac{\hbar^2 k^2}{2m}}}{(\pi v_{th}^2)^{3/2}} =$$

$$= \left(n \lambda_{th}^3\right) e^{-\beta \epsilon(k)} \quad (29) \quad \text{Maxwell's Distribution}$$

We will verify this in due course!