The slightly quantum ideal gas

Gabriel T. Landi

The ideal gas can be treated in at least 3 different levels:

- Classical ideal gas: we've done that already
- Slightly quantum ideal gas: use quantum mechanics but assumes that the particles are distinguishable
- Quantum ideal gas: takes into consideration the indistinguishability of the particles (quantum statistics)

We will do this one at the end of the course.

Mathematical warm-up: approximating sums by integrals

Before we start I want to show you a neat trick that is used extensively in statistical mechanics: how to approximate a sum by an integral. I will do this for a specific example: Stirling's formula for $\ln N!$ when N is large

we first write

$$\ln N! = \ln\left[N(N-1)(N-2)\dots 1\right]$$

$$= \ln N + \ln(N-1) + \dots + \ln(1)$$

$$= \sum_{m=1}^{N} \ln(m)$$

Assuming N is large, I want to approximate this sum by an integral. there is a trick to do this which always works: convert your sum to a Riemann sum

$$\int_a^b f(x)\,dx \approx \sum_{m=1}^{N} \Delta x\, f(x_m)$$

In our case we first define $x_m = \frac{m}{N}$. then we write

$$\ln N! = \sum_{m=1}^{N} \ln(N x_m) = N \ln N + \sum_{m=1}^{N} \ln x_m$$

Now we only need to worry about the last term. we first note that since $x_m = m/N$,

$$\Delta x = 1/N$$

thus when N is large, Δx will be tiny.

Now we multiply our sum by $1 = N\Delta x$

$$\sum_{m=1}^{N} \ln x_m = N \sum_{m=1}^{N} \Delta x \ln x_m$$

This has precisely the structure of a Riemann sum, so when N is large we may approximate

$$N \sum_{m=1}^{N} \Delta x \ln x_m \approx N \int_0^1 \ln x \, dx$$

the limits of integration are $m=1 \rightsquigarrow x_m = 1/N \approx 0$ and $m=N \rightsquigarrow x_m = 1$. this integral can be solved by integration by parts

$$\int_0^1 \ln x \, dx = \left[x \ln x - x \right] \Big|_0^1 = -1$$

thus we finally conclude that

$$\sum_{m=1}^{N} \ln (x_m) \approx -N$$

and therefore

$$\boxed{\ln N! \approx N \ln N - N} \qquad (0)$$

This is called <u>Stirling's formula</u>. Later on we will learn another technique that will give us an even better approximation.

We are interested in $N = 10^{23}$. For $N = 10^4$ the error is already in the order of 0.01%. Imagine for 10^{23}.

Schrödinger's Equation

The canonical way of formulating quantum mechanics is to promote observables to operators. The Hamiltonian of a particle in 1D is

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{1}$$

where now, the big difference is that $\hat{p}$ has been promoted to an operator

$$\hat{p} \rightarrow -i\hbar \frac{\partial}{\partial x} \tag{2}$$

[operators wear hats, like $\hat{H}$, $\hat{p}$, etc.]. Since $\hat{p}$ and $\hat{H}$ are operators, they must now act on something. This "something" is called a wave function $\psi(x)$. Thus

$$\hat{p}\,\psi = -i\hbar \frac{\partial \psi}{\partial x} = \text{some function} \tag{3}$$

Moreover

$$\hat{p}^2 = \left(-i\hbar \frac{\partial}{\partial x}\right)^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

Hence

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x)\,\psi(x)\right] \tag{4}$$

Operators act on wave functions to produce other wave functions. This is very much like matrices, which act on vectors to produce other vectors: $Ax = b$.

Of particular importance are those cases when the vector you produce is a multiple of the original vector.

$$Ax = \lambda x \tag{5}$$

In this case x is an eigenvector and λ is an eigenvalue. We do the same for operators

$$\hat{H}\psi = E\psi \tag{6}$$

ψ = eigen function

E = eigen energy = eigenvalue of $\hat{H}$

We can find eigenvalues and eigenvectors of any operator:

$$\hat{p}\psi = \lambda\psi \tag{7}$$

λ = eigenvalue of the momentum operator.

Explicitly Eq (7) reads

$$\hat{p}\psi = -i\hbar\frac{\partial\psi}{\partial x} = \lambda\psi$$

or

$$\frac{\partial\psi}{\partial x} = \frac{i\lambda\psi}{\hbar} \tag{8}$$

We are looking for a function ψ such that $\frac{\partial \psi}{\partial x}$ is a constant times itself. The answer is, of course, the exponential

$$\psi(x) = e^{i\lambda x/\hbar}$$

Then

$$\frac{\partial \psi}{\partial x} = \frac{i\lambda}{\hbar} e^{i\lambda x/\hbar} = \frac{i\lambda}{\hbar}\psi$$

Thus, we have just found the eigenfunctions of the operator $\hat{p}$. It is convenient to write these eigenfunctions as

$$\psi_k(x) = e^{ikx} \tag{9}$$

Then

$$\hat{p}\,\psi_k(x) = -i\hbar \frac{\partial \psi_k}{\partial x} = -i\hbar\,(ik)\,e^{ikx} = \hbar k\,\psi_k(x)$$

or

$$\boxed{\hat{p}\,\psi_k(x) = \hbar k\,\psi_k(x), \quad \psi_k(x) = e^{ikx}} \tag{10}$$

The eigenvalues of $\hat{p}$ are $\hbar k$, where k can be any real number. We have a continuum of eigenvalues. I know that may sound weird at first, but there is nothing wrong about it.

The quantity k has units of 1/length. We say it has units of <u>wave-number</u> or <u>wave-vector</u>. Then $\hbar k$ has units of momentum.

If a system is in a state described by a wave-function $\psi(x)$, the prob. distribution (PDF) of finding it somewhere is

$$P(x) = |\psi(x)|^2 \tag{11}$$

Thus, we must have the normalization condition

$$\int_{-\infty}^{\infty} dx \, |\psi(x)|^2 = 1 \tag{12}$$

The momentum eigenfunctions $\psi_k(x)$ in Eq (10) do not satisfy this property because

$$\int_{-\infty}^{\infty} dx \, |e^{ikx}|^2 = \int_{-\infty}^{\infty} dx \; 1 = \infty$$

This is annoying. We didn't make any mistakes. This is simply a mathematical property of the system: e^{ikx} is a plane wave and plane waves extend over all of space.

There is a trick to get rid of this annoying feature; we assume the particle is actually in a box of length L with <u>periodic boundary conditions</u> (PBC)

$$\boxed{\psi(x+L) = \psi(x)} \tag{13}$$

PBC's maintain translation invariance, which is always very convenient. Normalization is now modified to

$$\int_0^L |\psi(x)|^2 dx = 1$$

In the case of the momentum eigenfunctions $\psi_k(x) = e^{ikx}$, we will then have

$$\int_0^L |e^{ikx}| dx = \int_0^L dx = L$$

Thus, we see that to obtain a correct normalization we should have

$$\boxed{\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}} \qquad (14)$$

Now let us look at condition (13) of the PBC:

$$\psi_k(x+L) = \frac{1}{\sqrt{L}} e^{ik(x+L)} = \frac{1}{\sqrt{L}} e^{ikx} = \psi_k(x)$$

Thus, we see that we must have

$$e^{ikL} = 1 \qquad (15)$$

PBCs impose a condition on the allowed values of k. Eq (15) will be satisfied when

$$kL = 2\pi n, \quad n = 0, \pm 1, \pm 2, \ldots$$

or

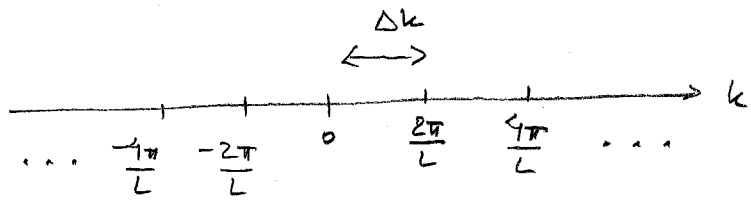
$$\boxed{k = \frac{2\pi m}{L}, \qquad m = 0, \pm 1, \pm 2, \ldots} \tag{16}$$

The momentum eigenvalues $\hbar k$ are now <u>quantized</u>. Their spacing is

$$\Delta k = \frac{2\pi}{L} \tag{17}$$

so if L is large they will be very closely spaced.

Allowed k values :



This quantization is a <u>Mathematical trick</u> (like the PBC). But it is a very convenient one. Everyone uses it. Even if you look at very advanced condensed matter or particle physics books, everyone quantizes the momentum eigenvalues like this.

In summary, we have

$$\boxed{\begin{aligned} &\hat{p}\psi_k = \hbar k \psi_k \\ &\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx} \\ &k = \frac{2\pi m}{L}, \quad m = 0, \pm 1, \pm 2, \ldots \end{aligned}} \tag{18}$$

Now let us look at the energy of the particle in a box. The Hamiltonian is given in (5) with $V(x) = 0$. (this is a free particle, except for the box):

$$\hat{H} = \frac{\hat{p}^2}{2m} \tag{19}$$

Now we want to find its eigenvalues and eigenfunctions

$$\hat{H}\psi = E\psi \tag{20}$$

Well, its our lucky day: we already know the eigenfunctions.

In linear algebra, if x is an eigenvector of A

$$Ax = \lambda x$$

and if $B = cA^2$, where c is a constant, then

$$Bx = cA^2x = cA(Ax) = cA(\lambda x) = c\lambda(Ax) = c\lambda^2 x$$

Thus

$$Bx = (c\lambda^2)x$$

the eigenvector of cA^2 is also x and the eigenvalue is $c\lambda^2$.

Now we go back to (19) and use (18)

$$\hat{H}\psi_k = \frac{\hat{p}^2}{2m}\psi_k = \frac{\hat{p}}{2m}(\hat{p}\psi_k) = \frac{\hat{p}}{2m}(\hbar k \psi_k)$$

$$= \frac{\hbar k}{2m}(\hat{p}\psi_k) = \frac{(\hbar k)^2}{2m}\psi_k$$

Thus we conclude that $\psi_k = \frac{1}{\sqrt{L}} e^{ikx}$ is also an eigenfunction of $\hat{H} = \hat{p}^2/2m$, with eigenenergies

$$\boxed{E_k = \frac{\hbar^2 k^2}{2m}} \tag{21}$$

Notice how this is only true when there is no potential energy. If $V(x) \neq 0$ then

$$\hat{H}\psi_k = \left[\frac{\hat{p}^2}{2m} + V(x)\right]\psi_k = \underbrace{\left[\frac{\hbar^2 k^2}{2m} + V(x)\right]}_{\text{This is not a number! It is a function of } x.} \psi_k$$

For a free particle the energy (21) is just the kinetic energy. There is no potential energy.

Eq (21) is our first example of a <u>dispersion relation</u>

$$\boxed{\text{Dispersion relation} = \text{energy - momentum relation}} \tag{22}$$

Eq (21) corresponds to a non-relativistic dispersion relation

$$E = \frac{p^2}{2m} \qquad (p = \hbar k) \tag{23}$$

Another common dispersion relation is that of photons

$$\omega = c\,|k| \tag{24}$$

In this case we write ω and k, but that is the same as E and p.

$$\boxed{\begin{aligned} E &= \hbar\omega \\ p &= \hbar k \end{aligned}}$$

$$\therefore \boxed{\omega = c|k| \quad \text{is the same as} \quad E = c\,|p|} \tag{25}$$

This is a <u>ultra-relativistic relation</u>, or a <u>massless relation</u>.

In general we can have something in between (23) and (25),

$$\boxed{E = \sqrt{m^2c^4 + p^2c^2}} \tag{26}$$

This reduces to (23) when $pc \ll mc^2$ and to (25) when $pc \gg mc^2$.

In condensed matter we find that the presence of the atoms changes the dispersion relations of the electrons. And it can do so in some quite weird ways. A simple example that appear all the time is

$$E = \text{const} \times (1 - \cos ka) \tag{27}$$

where a is the lattice constant. If $ka \ll 1$ this becomes approximately $E \sim k^2$. But for large ka it is quite different

An extreme and beautiful example is <u>graphene</u>, a 2D sheet of carbon. The interaction of the electrons with the ions of C is so peculiar that it changes its dispersion relation from (23) to (25).

$$\boxed{\text{electron in graphene}: \quad E \simeq \text{const} \times |p|} \tag{28}$$

Electrons in graphene move approximately like massless particles! Practically all of the special properties of graphene follow from this fact.

Extension to 3D

It is quite easy to extend all our previous calculations to 3D. The Hamiltonian will now read

$$\hat{H} = \frac{\hat{p}^2}{2m} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} \tag{29}$$

The eigenfunctions of each momenta are just like Eq (18), so the simultaneous eigenfunctions of all 3 components will be

$$\boxed{\psi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{x}}} \tag{30}$$

where $V = L^3$ is the volume of the box. This function satisfies

$$\hat{p}_i \psi_{\mathbf{k}}(\mathbf{x}) = \hbar k_i \psi_{\mathbf{k}}(\mathbf{x}), \quad i = x, y, z \tag{31}$$

Moreover

$$k_i = \frac{2\pi}{L} n_i, \qquad n_i = 0, \pm 1, \pm 2, \pm 3, \ldots \tag{32}$$

so we have independent integers n_x, n_y, n_z for each direction.

Finally

$$\hat{H}\psi_{\mathbf{k}} = E_{\mathbf{k}}\psi_{\mathbf{k}}$$

where

$$\boxed{E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)} \tag{33}$$

Thus, the energies depend on the 3 quantum numbers (k_x, k_y, k_z).

The partition function

Now that we know the energies $E_{\mathbf{k}}$ we may see what happens if we put this one particle in a box connected to a bath at a temperature T.

The partition function is

$$Z_1 = \sum_{k_x, k_y, k_z} e^{-\beta E_{\mathbf{k}}} = \sum_{k_x, k_y, k_z} e^{-\beta \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)} \tag{34}$$

or

$$Z_1 = \left[\sum_{k_x} e^{-\beta \hbar^2 k_x^2/2m} \right] \left[\sum_{k_y} e^{-\beta \hbar^2 k_y^2/2m} \right] \left[\sum_{k_z} e^{-\beta \hbar^2 k_z^2/2m} \right]$$

the 3 sums are actually equal. We may compute them by approximating them to an integral. To do that we use the fact that

$$k_x = \frac{2\pi n_x}{L}$$

so

$$\Delta k_x = \frac{2\pi}{L}$$

when L is large, Δk_x will be tiny. So we may multiply the sum by $1 = \frac{L}{2\pi}\Delta k_x$ and write

$$\sum_{k_x} e^{-\beta \hbar^2 k_x^2/2m} = \frac{L}{2\pi} \sum_{k_x} \Delta k_x \, e^{-\beta \hbar^2 k_x^2/2m}$$

$$\approx \frac{L}{2\pi} \int_{-\infty}^{\infty} dk_x \, e^{-\beta \hbar^2 k_x^2/2m}$$

This is a Gaussian integral. Recall that

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \tag{35}$$

we then get

$$\sum_{k_x} e^{-\beta \hbar^2 k_x^2/2m} = \frac{L}{2\pi}\left[\frac{2m\pi}{\beta\hbar^2}\right]^{1/2}$$

Since the 3 integrals are identical we then get

$$\boxed{z_1 = \frac{V}{(2\pi\hbar)^3}(2\pi m k_B T)^{3/2}} \tag{36}$$

where $V = L^3$.

When we studied the ideal gas classically we found a very similar result

$$z_1^c = V(2\pi m k_B T)^{3/2} \tag{37}$$

The only difference now is the appearance of the term $(2\pi\hbar)^3 = h^3$. This actually has a physical interpretation.

In the classical case we usually write

$$z_1^c = \int e^{-\beta H} d^3r\, d^3p \tag{38}$$

This is somewhat awkward because Z_1^c has units. In fact, recall that $[xp] = [h]$ so Z has units of h^3. The reason why this is weird is because $F = -k_B T \ln Z$ and usually we don't like to deal with the logarithm of something dimensional.

In the quantum case we don't have this problem because

$$Z_1^Q = \sum_n e^{-\beta E_n}$$

so Z is dimensionless.

This discussion suggests interpreting h^3 as the basic unit of volume in phase space: $d^3r\, d^3p \sim h^3$. This is corroborated by the Heisenberg uncertainty principle, which states that $\Delta x \Delta p \sim h$

Many people like to correct this deficiency "by hand", redefining the classical partition function as

$$Z_1^c = \int e^{-\beta H} \frac{d^3r\, d^3p}{h^3} \qquad (39)$$

so that now it is dimensionless.

Personally I am not a big fan of this. If you don't want the deficiencies of the classical theory, then simply use the quantum theory. Amending the classical theory by hand makes the calculations seem arbitrary and also causes confusion with the interpretation of Z as a normalization constant for the PDF.

Note also that this does not affect the internal energy or the heat capacity. It only introduces a constant term in the free energy and the entropy.

The density of states

Now I want to compute Z again using another method. The result is of course the same, but this method will be usefull in other problems we will deal with later on.

The partition function is

$$Z_1 = \sum_{k_x, k_y, k_z} e^{-\beta E_k}$$

Note that the k's only appear in the sum through the particular combination $E_k = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$. The idea is to convert the sum over (k_x, k_y, k_z) into an integral over E [since the k vary quasi-continuously, then so will E].

That is, in general we want to approximate, for an arbitrary $f(E_k)$

$$\boxed{\sum_{k_x, k_y, k_z} f(E_k) \approx \int_0^\infty D(E) f(E)\, dE} \qquad (40)$$

The function $D(E)$ that we pick up in the middle is called the <u>density of states</u> (DOS)

To find $D(E)$ we proceed as before.

$$\sum_{k_x,k_y,k_z} f(E_{\mathbf{k}}) = \left(\frac{L}{2\pi}\right)^3 \sum_{k_x,k_y,k_z} \Delta k_x \Delta k_y \Delta k_z \, f(E_{\mathbf{k}})$$

$$= \frac{V}{(2\pi)^3} \int d^3\mathbf{k} \; f(E_{\mathbf{k}})$$

Now we note that $E_{\mathbf{k}}$ depends only on $|\mathbf{k}|$. So we convert to polar coordinates:

$$d^3\mathbf{k} = k^2 dk \, d\Omega$$

where Ω is the solid angle. We then get

$$\sum_{k_x,k_y,k_z} f(E_{\mathbf{k}}) = \frac{V}{(2\pi)^3} \underbrace{\int d\Omega}_{4\pi} \int dk \, k^2 \, f(E_k)$$

Lastly we change variables from k to $E = \frac{\hbar^2 k^2}{2m}$. We then get

$$k = \left(\frac{2m}{\hbar^2}\right)^{1/2} \sqrt{E} \qquad dk = \left(\frac{2m}{\hbar^2}\right)^{1/2} \frac{1}{2}\frac{1}{\sqrt{E}}$$

$$\therefore \; dk \, k^2 = \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{2}\frac{1}{\sqrt{E}} \, E$$

$$= \frac{1}{2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{E}$$

Thus

$$\sum_{k_x,k_y,k_z} f(E_{\mathbf{k}}) = \frac{V}{(2\pi)^3} 4\pi \, \frac{1}{2} \frac{(2m)^{3/2}}{\hbar^3} \int_0^\infty dE \, \sqrt{E} \, f(E)$$

Comparing with (40) we may read off the density of states

$$\boxed{D(E) = \frac{V}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{E}} \tag{41}$$

The density of states, as its name implies, gives the density of allowed quantum states around the energy E

Our result shows that the higher in the energy E, the larger is the number of allowed states.

The partition function may now be written as

$$Z_1 = \int_0^\infty e^{-\beta E} D(E)\, dE \tag{42}$$

Just as a sanity check:

$$Z_1 = \frac{V}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \underbrace{\int_0^\infty e^{-\beta E} \sqrt{E}\, dE}_{\frac{\sqrt{\pi}}{2\beta^{3/2}}} =$$

$$= \frac{V}{8\pi^{3/2}} \frac{(2m)^{3/2}}{\hbar^3} \frac{1}{\beta^{3/2}} = \frac{V}{(2\pi\hbar)^3} (2\pi m k_B T)^{3/2}$$

which is Eq (36).

Ideal gases with internal structure

The partition function of a gas of N particles is

$$Z = Z_1^N = \frac{V^N}{(2\pi\hbar)^{3N}} (2\pi m k_B T)^{3N/2} \tag{43}$$

the internal energy is therefore

$$U = -\frac{\partial}{\partial\beta} \ln Z = -\frac{3N}{2} \frac{\partial}{\partial\beta} \ln(1/\beta) = -\frac{3N}{2}\left(-\frac{1}{\beta}\right)$$

or

$$U = \frac{3N}{2} k_B T \tag{44}$$

thus the heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{3N}{2} k_B$$

and the specific heat is

$$c = \frac{C}{N} = \frac{3}{2} k_B \tag{45}$$

The specific heat of an ideal gas is 3/2 of k_B. Here are some experimental results at $T = 300K$

	He	Ar	Xe	Kr
c (J/mol K)	12.5	12.5	12.7	12.3
c/k_B	1.503	1.503	1.528	1.480

We see that the results for the monoatomic gases are all very close to 3/2. But here is some data for diatomic gases

	H_2	CO	N_2	Cl_2
c (J/mol K)	20.18	20.2	19.9	24.1
c/k_B	2.427	2.43	2.39	3.06.

(T=300K)

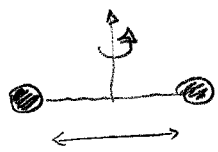
the values are now higher than 3/2.

These gases can still be considered ideal: an ideal gas is one where you can neglect the <u>interactions</u> between the molecules (so H only has a kinetic energy). And you can always ensure that this is the case by taking measurements on a sufficiently rarified gas.

Thus, the change in c from the monoatomic to the diatomic gases is not due to interactions between the molecules. It must therefore come from their <u>internal structure</u>

So far we have treated our molecules as point particles but that is not true. They also have internal degrees of freedom, related to the motion of the protons, neutrons and electrons.

The diatomic molecules, in particular, may <u>vibrate</u> and <u>rotate</u>



It is these extra degrees which are responsible for the change in c.

But before we study rotations and vibrations in more detail, let us think about the degrees of freedom of the monoatomic gases. After all, they are composed of electrons that may store thermal energy by populating excited states. But why don't we see this in the specific heat?

To answer this consider again the two-state system

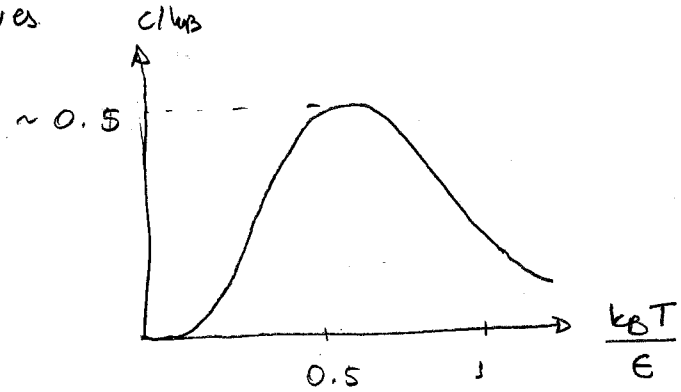
$$\text{———} \quad E_1 = \epsilon$$

$$\text{———} \quad E_0 = 0$$

We have seen that the heat capacity of this system is given by

$$C = k_B \left(\frac{\epsilon}{k_B T}\right) \frac{e^{\epsilon/k_B T}}{(e^{\epsilon/k_B T}+1)^2} \tag{46}$$

A plot of this gives



What we see is that, when $\frac{k_B T}{\epsilon} \ll 1$ the specific heat is negligible. This is intuitive: when $k_B T/\epsilon \ll 1$ the excited state is practically unpopulated so the system cannot store thermal energy.

In fact, when $\frac{\epsilon}{k_B T} \gg 1$ we may approximate

$$c \simeq k_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{e^{\epsilon/k_B T}}{(e^{\epsilon/k_B T})^2} = k_B \left(\frac{\epsilon}{k_B T}\right)^2 e^{-\epsilon/k_B T}$$

The pre-factor $(\epsilon/k_B T)^2$ is not important. The dependence on the exponential is much stronger

$$\boxed{c \sim e^{-\epsilon/k_B T} \quad \text{when} \quad \frac{k_B T}{\epsilon} \ll 1} \tag{47}$$

If the thermal energy $k_B T$ is much smaller than the excitation energy ϵ, the heat capacity is <u>exponentially</u> suppressed.

In order to get a meaningful heat capacity we must have $k_B T \sim \epsilon$. It is useful to know that

$$\boxed{T = 300\ \text{K} \rightsquigarrow k_B T = 0.026\ \text{eV}} \tag{48}$$

The typical energy level separations in a atomic system are of the order of 1 eV. Thus

$$\frac{k_B T}{\epsilon} \sim 0.026$$

If we plug this in Eq (46) we get

$$\frac{c}{k_B} \sim 10^{-14}$$

This shows why the electronic levels do not contribute to the specific heat.

For the kinetic energy we don't have this kind of problem. Recall that

$$E = \frac{\hbar^2 k^2}{2m}$$

So the typical spacings of the kinetic energy levels are related to the spacings $\Delta k = 2\pi/L$. Since L is large, these spacings are negligible. Thus the energy levels of the kinetic energy form a quasi-continuum ($\epsilon \sim 0$), making it very easy to populate the excited states.

Now let us look at the vibration of molecules. This vibration is just like a harmonic oscillator, so we know that the energy levels will be of the form

$$E_{vib} = \hbar\omega(n + 1/2) \quad , n = 0, 1, 2, \ldots$$

For the CO molecule

$$\hbar\omega \sim 0.2 \text{ eV} \qquad (\text{CO molecule})$$

The typical energy spacing is $\epsilon = \Delta E_{vib} = \hbar\omega$. Thus at $T = 300$ K we will have

$$\frac{k_B T}{\hbar\omega} \simeq \frac{0.026}{0.2} \simeq 0.13$$

The heat capacity of the QHO is similar to (46)

$$C = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \tag{49}$$

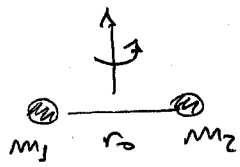
Plugging our value we get $C \sim 0.027$. [You get the same value if you use (46)]. Thus we see that at $T = 300\,K$ the vibration of the diatomic molecules also contribute negligibly to the specific heat [Remember from our tables that $C_{CO} \sim 2.5\, k_B$, whereas the kinetic energy only contributes 1.5].

Since the vibrations do not contribute, the main contribution to C must come from the <u>rotations</u>. The energy of rotations of a system with angular momentum L is

$$E_{rot} = \frac{L^2}{2I} \tag{50}$$

where I is the moment of inertia

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 \tag{51}$$



For the CO molecule we have

$$m_1 = m_C = 12 \frac{g}{mol}$$

$$m_2 = m_O = 16\ g/mol$$

$$\frac{m_1 m_2}{m_1 + m_2} \simeq 6.9 \frac{g}{mol} \rightsquigarrow \frac{6.9}{6.\times 10^{23}} \times 10^{-3} \simeq 1.15 \times 10^{-26}\, kg$$

Moreover, for CO, $r_0 \approx 113$ pm $= 1.13 \times 10^{-10}$ m. Thus

$$I \simeq 1.5 \times 10^{-46} \text{ kg m}^2$$

In quantum mechanics we learn that the eigenvalues of the angular momentum operator $\hat{L}^2$ are

$$\text{eigs}(\hat{L}^2) = \hbar^2 \ell(\ell+1), \quad \ell = 0, 1, 2, \ldots$$

Thus, Eq (50) must be replaced by

$$E_{rot} = \frac{\hbar^2}{2I} \ell(\ell+1)$$

Now: $[\hbar] = J.s = \text{kg m}^2/s$, so

$$\left[\frac{\hbar^2}{I}\right] = \text{kg}^2 \frac{m^4}{s^2} \frac{1}{\text{kg m}^2} = \text{kg}^2 \frac{m^2}{s^2} = J$$

We have, for the CO molecule

$$\frac{\hbar^2}{2I} = \frac{(1.054 \times 10^{-34})^2}{1.5 \times 10^{-46}} \simeq 3.7 \times 10^{-23} \text{ J}$$

or, in eV (divide by 1.6×10^{-19})

$$\frac{\hbar^2}{2I} \simeq 0.00023 \text{ eV} \tag{52}$$

We therefore see that the typical rotation energies are much smaller than the typical vibrational energies. Moreover, they are also much smaller than $k_B T \sim 0.026$ eV, so at room temperature there will be a significant amount of energy stored in the rotations and practically none stored in the vibrations

Calculation of the rotational contribution to the specific heat

The energy from the rotations is

$$E_\ell = \frac{\hbar^2}{2I}\,\ell(\ell+1)\,, \quad \ell = 0, 1, 2, \ldots \tag{53}$$

But these energies are degenerate because angular momentum is also characterized by the quantum number

$$m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell \tag{54}$$

Thus, each E_ℓ is $(2\ell+1)$-fold degenerate. The rotational contribution to the partition function will then be

$$Z_{rot} = \sum_{\ell, m_\ell} e^{-\beta E_\ell} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\beta E_\ell} \tag{55}$$

or

$$Z_{rot} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\frac{\beta\hbar^2}{2I}\ell(\ell+1)} \tag{66}$$

this sum unfortunately cannot be computed analytically. But from (52) we know that

$$\frac{\beta\hbar^2}{2I} \simeq \frac{0.00023}{0.026} \simeq 0.0088 \ll 1 \tag{67}$$

Thus we may try to approximate the sum to an integral

To do that we set

$$x_\ell = \frac{\beta\hbar^2}{2I}\,\ell(\ell+1)$$

then, since $\Delta\ell = 1$, we will have

$$\Delta x_\ell = \frac{\beta\hbar^2}{2I}\left[(\ell+1)(\ell+2) - \ell(\ell+1)\right]$$

$$= \frac{\beta\hbar^2}{2I}\,2(\ell+1) \ll 1 \quad \text{because} \quad \frac{\beta\hbar^2}{2I} \ll 1.$$

we now insert the convenient "1" in (66)

$$1 = \frac{\Delta x_\ell}{2(\ell+1)}\,\frac{2I}{\beta\hbar^2}$$

we then get

$$Z_{rot} = \frac{2I}{\beta\hbar^2}\sum_{\ell=0}^{\infty}\frac{(2\ell+1)}{2(\ell+1)}\,e^{-x_\ell}\,\Delta x_\ell$$

we may approximate

$$\frac{2\ell+1}{2(\ell+1)} \sim 1$$

so that

$$Z_{rot} = \frac{2I}{\beta\hbar^2}\sum_{\ell}\Delta x_\ell\, e^{-x_\ell}$$

$$\simeq \frac{2I}{\beta\hbar^2}\underbrace{\int_0^\infty dx\, e^{-x}}_{1}$$

$$\therefore \quad \boxed{Z_{rot} = \frac{2I}{\beta\hbar^2}} \qquad (68)$$

the average energy due to rotations will be

$$U_{rot} = -\frac{\partial}{\partial \beta} \ln Z_{rot} = -\frac{\partial}{\partial \beta} \ln (1/\beta) = \frac{1}{\beta} = k_B T \qquad (69)$$

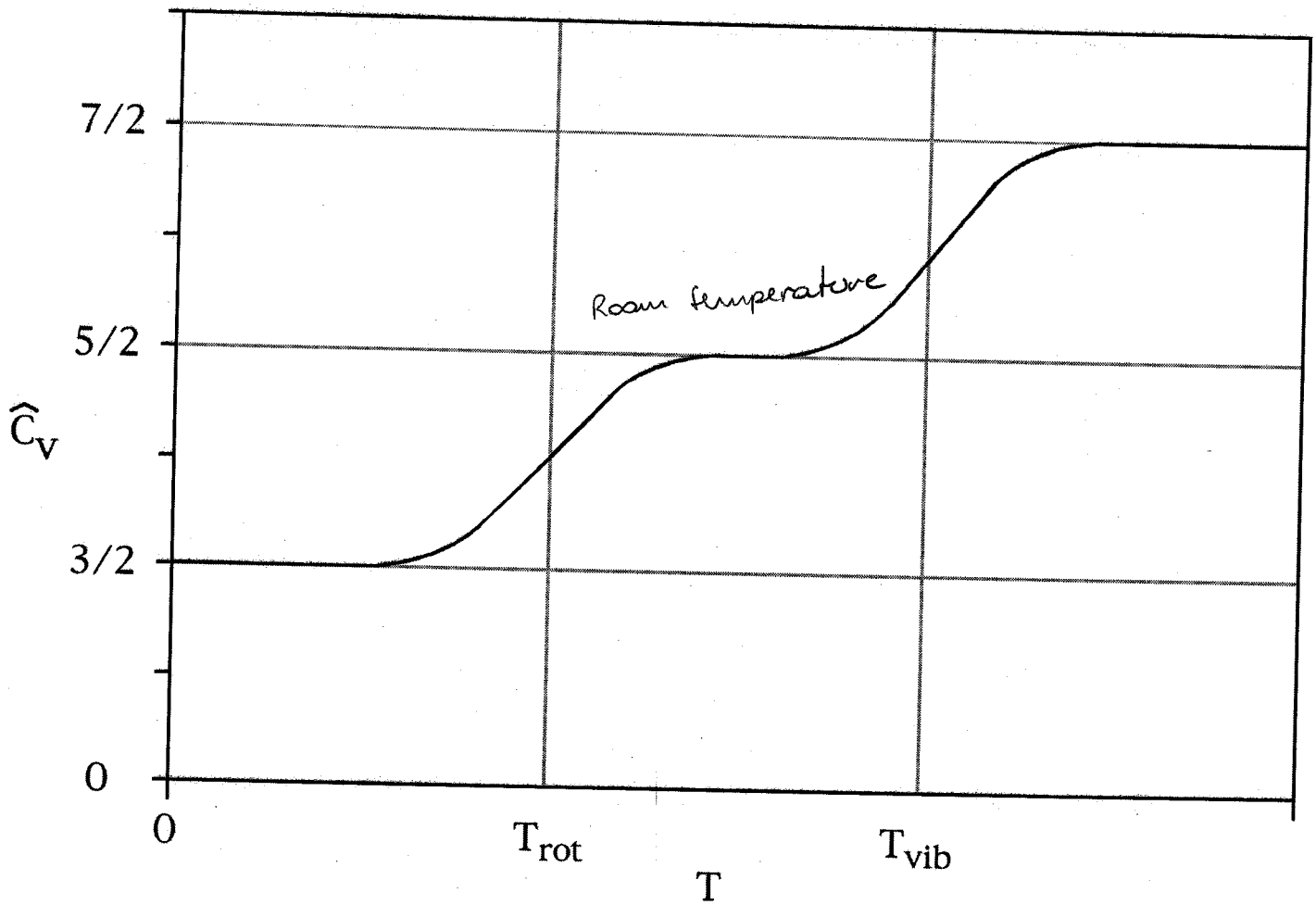
Thus, the specific heat contribution due to the rotations will be

$$C_{rot} = \frac{\partial U_{rot}}{\partial T} = k_B \qquad (70)$$

The total specific heat of the diatomic molecule will then be

$$C = \frac{3}{2} k_B + k_B = \frac{5}{2} k_B \qquad (71)$$

This agrees very well with the experimental results.



the vibrations at very high T also contribute 1 k_B to c.

Specific Heat of Al

N. E. Phillips, Phys Rev 114, 676 (1959)

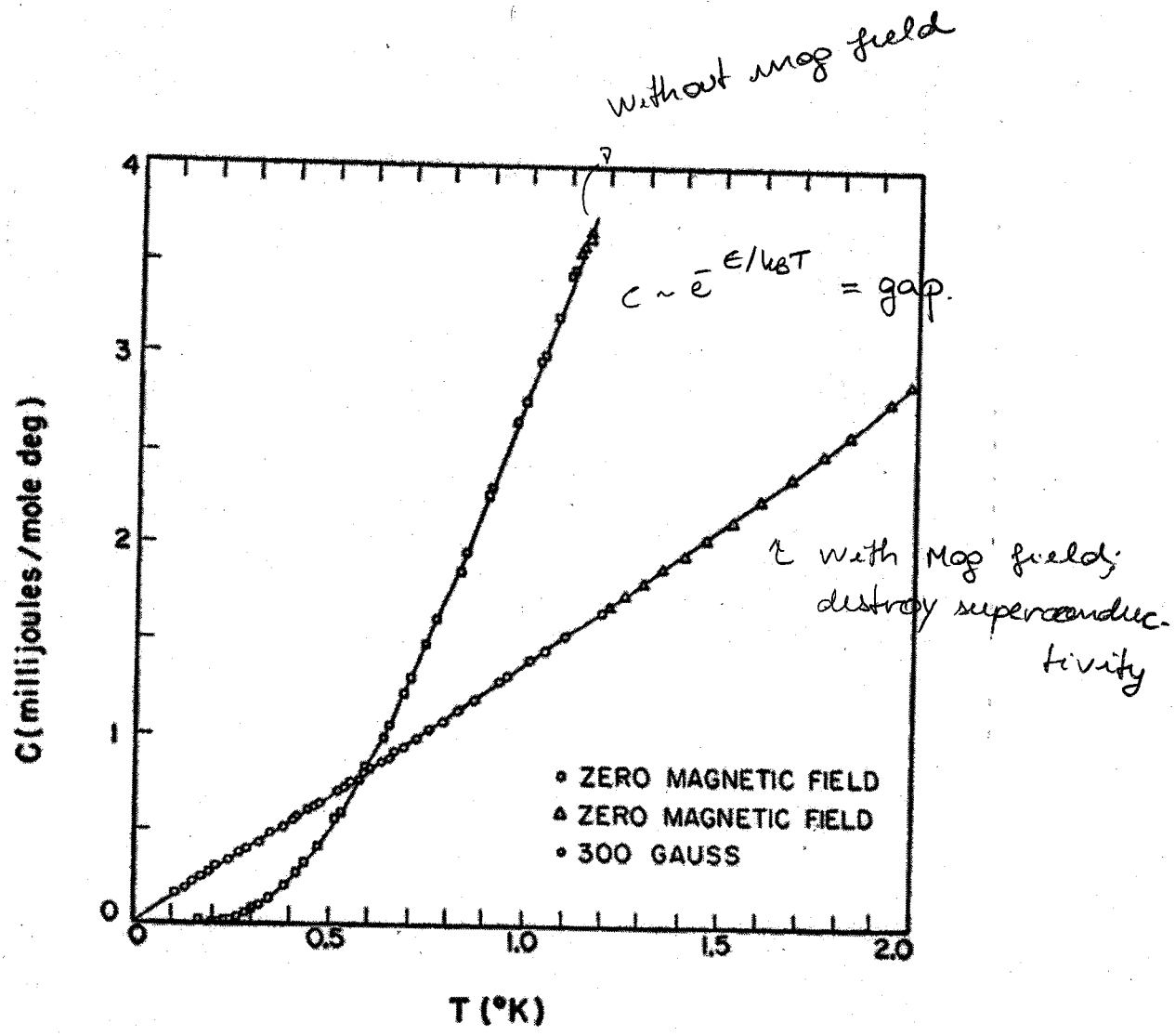


FIG. 4. Heat capacity of aluminum from 0.1 to 2.0°K. The two experiments in the adiabatic demagnetization range are designated by squares for the normal state and circles for the superconducting state. The triangles represent points taken at liquid helium temperatures.

The Gibbs paradox

Now let's talk about entropy. We have, for the monoatomic ideal gas,

$$Z = \frac{V^N}{h^{3N}} (2\pi m k_B T)^{3N/2}$$

$$U = \frac{3}{2} N k_B T$$

$$F = -N k_B T \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right]$$

$$\therefore \quad S = \frac{U - F}{T} = \frac{3}{2} N k_B + N k_B \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right] \tag{72}$$

Or we may also write

$$\boxed{S = N k_B \ln V + \frac{3}{2} N k_B \left\{ 1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right\}} \tag{73}$$

The energy is an extensive quantity

$$U(\alpha N, \alpha V) = \alpha U(N, V) \tag{74}$$

But the same is not true for S because of the term $\ln V$.

Thus, the entropy of an ideal gas is not extensive

Boltzmann was the first to realize that you could fix this by <u>hand</u> if we subtract from S a term $-k_B \ln N!$. Or, using Stirling's formula ($\ln N! \simeq N \ln N - N$)

$$- k_B N \ln N + k_B N$$

We then get, instead of (73)

$$\boxed{S = N k_B \ln(V/N) + \frac{5}{2} N k_B + \frac{3}{2} N k_B \ln\left(\frac{2\pi m k_B T}{h^2}\right)} \qquad (75)$$

This formula is now extensive

$$S(\alpha N, \alpha V) = \alpha N k_B \ln\left(\frac{\alpha V}{\alpha N}\right) + \frac{5}{2}(\alpha N) k_B + \frac{3}{2}(\alpha N) k_B \ln\left(\frac{2\pi m k_B T}{h^2}\right)$$

$$= \alpha S(N, V)$$

Now let's try to understand the physical meaning of this term $k_B \ln N!$ We will learn that it is related to the fact that the particles are <u>indistinguishable</u>

Consider a system of N particles. Let

$$y_i = (r_i, p_i) \tag{76}$$

denote the microstate of particle i. the Gibbs probability is

$$P(y_1, \dots, y_N) = \frac{e^{-\beta H(y_1, \dots, y_N)}}{Z} \tag{77}$$

where

$$Z = \int e^{-\beta H} \, Dy_1 \dots Dy_N \tag{78}$$

We have constructed thermodynamics by associating Z to the free energy $F = -k_B T \ln Z$.

But, in practice, $P(y_1, \dots, y_N)$ is not experimentally accessible:

$P(y_1, y_2, y_3)$ = Prob that particle 1 is at y_1, particle 2 is at y_2 and particle 3 is at y_3.

what we can actually know is

Prob. one particle is at y_1, another at y_2 and another at y_3.

The particles are indistinguishable so we cannot label them. All we can say is that one particle is in this state, another in that state and so on.

So, to be precise, the P in Eq (77) could be written as

$$P(1 \to y_1,\ 2 \to y_2,\ 3 \to y_3)$$

the actual probability is, for instance if $N = 3$

$$\begin{aligned}
\text{Prob(undistinguishable)} = {} & P(1 \to y_1,\ 2 \to y_2,\ 3 \to y_3) + \\
& + P(1 \to y_1,\ 2 \to y_3,\ 3 \to y_2) \\
& + P(1 \to y_2,\ 2 \to y_1,\ 3 \to y_3) \\
& + P(1 \to y_3,\ 2 \to y_2,\ 3 \to y_1) \\
& + P(1 \to y_2,\ 2 \to y_3,\ 3 \to y_1) \\
& + P(1 \to y_3,\ 2 \to y_1,\ 3 \to y_2)
\end{aligned}$$

there are in total $3! = 6$ ways of putting the 3 particles in the 3 microstates. This new prob is no longer normalized, so we should divide by $1/3!$ or, more generally, $1/N!$

The actual partition function will therefore pick up a factor of $1/N!$

$$\boxed{Z = \frac{Z_1^N}{N!}} \qquad (79)$$

Consequently

$$F = -Nk_BT \ln Z_1 + k_BT \ln N!$$

and therefore

$$S = \frac{U-F}{T} = (\ldots) - k_B \ln N!$$

which is Boltzmann's factor.

Thus, we conclude that, whenever we are dealing with indistinguishable particles, the partition function should pick-up a factor of $1/N!$ to account for the correct counting of the states.