

Physics 112 : Lecture 9

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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September 21, 2017

1 Ideal Gases

¹ We know from Quantum Mechanics that a particle trapped inside a cubical box with side length L has quantized energy levels given by:

$$\epsilon_n = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2)$$

where n_x, n_y, n_z range from $1, 2, \dots, \infty$ and $n^2 = n_x^2 + n_y^2 + n_z^2$. It might seem that this is too simplistic a model to really model anything useful; but if you think about it, a gas is comprised of molecules that are trapped inside a large box (the room)! So if we can understand this system, we can in principle understand gases. You might also wonder that we seem to only be treating the cubical box case; but this is not really that big of an issue; you can treat arbitrary rectangular prisms with just a few minor tweaks in what follows.

So we can write down our partition function for a single particle:

$$Z = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2) / 2mL^2 \tau}$$

Now there are two 'limiting cases' that we are interested in, one where the thermal energy (dictated by τ) is much larger than the spacing of the energy levels, and one where the thermal energy is much smaller than the spacing of the energy levels. When τ is much larger, we can treat the energy levels as a continuum and perform integrals to drastically simplify the partition function, but when τ is much smaller; then we can simply truncate the sum after a few terms, because the particles will never be excited beyond the first few energy levels.

In the limit where τ is much larger than the energy levels, we mean:

$$\Delta n^2 \ll \frac{2mL^2 \tau}{\hbar^2 \pi^2}$$

so

¹Sorry this is a bit late

$$1 \ll \frac{2mL^2\tau}{\hbar^2\pi^2}$$

and, by substituting in $E = 3\tau/2$, $E = p^2/2m$, we find that:

$$\frac{h}{p} \ll L$$

(up to a constant), where h/p is the de Broglie wavelength of the particle. All this is saying is that we are justified in our assumption that τ is much larger than the spacing of the energy levels when it happens that the de Broglie wavelength of the particles in the box are much smaller than the scale of the box itself, which makes sense. In this limit, we can calculate the partition function:

$$Z = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z e^{-\alpha^2(n_x^2+n_y^2+n_z^2)}$$

where

$$\alpha^2 = \frac{\hbar^2\pi^2}{2mL^2\tau}$$

But these are just Gaussian integrals, so we can evaluate them to find that:

$$Z = n_Q V$$

where V is the volume of the box, and n_Q , the 'quantum concentration' of the system, is defined to be:

$$n_Q = \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2}$$

Physically, we can understand the 'quantum concentration' as the number of particles in the box per unit volume, where the unit volumes are defined to be the de Broglie wavelength cubed. The intuition behind this is that since particles behave like waves in some sense, they cannot be localised in space more than their de Broglie wavelength, so this is a natural scale to use to finitely 'partition' the space inside the box.

Now, we can find the energy of the system:

$$U = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau} \right) = \tau^2 \left(\frac{3}{2} \frac{1}{\tau} \right) = \frac{3}{2} \tau$$

which is a result we know and love.

2 Multiple Particles

If we had N particles, separated into N different boxes, then the partition function for the whole system Z_N would be given by $Z_N = Z_1^N$ where Z_1 is the partition function for a single particle in a single box. The situation is different when all the N particles are in the same

box however, since when they were in separate boxes they were distinguishable, but in the same box *they are indistinguishable*. So we have overcounted the partition function by $N!$, the number of ways of permuting the particles. Hence we have a partition function:

$$Z_N = \frac{1}{N!} Z_1^N = \frac{1}{N!} (n_Q V)^N$$

If we now calculate the energy for the entire system, we have:

$$U = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau} \right) = \frac{3}{2} \tau$$

as expected. Now, we can use all the other tools we have to find out more about ideal gases, for instance our helmholtz free energy is given by:

$$F = -\tau \ln Z_n = \tau N \ln \left(\frac{n}{n_Q} \right) - \tau N$$

where $n = N/V$ is the "classical concentration" as opposed to the "quantum concentration". We can now consider the pressure:

$$P = \left(\frac{\partial F}{\partial V} \right)_\tau = \frac{N}{V} \tau$$

And with this, we have derived:

$$PV = N\tau$$

It's the ideal gas law! We can find the entropy of the system as well:

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_V = N \left[\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right]$$

3 Quadratic Degrees of Freedom

So far, we have only really been considering the translational degrees of freedom, when considering the energy levels of particles in a box. But molecules have other degrees of freedom, for instance rotational and vibrational degrees of freedom. Generally, these degrees of freedom are 'quadratic', in the sense that if q and p are coordinates that represent two quadratic degrees of freedom, then:

$$E(q, p) = \alpha q^2 + \beta p^2$$

In this case, when we calculate the partition function for the system, assuming that the thermal energy is much larger than the spacing between the energy levels we have:

$$Z = \sum_{q,p} e^{-E(q,p)/\tau} = \frac{1}{h} \int_{-\infty}^{\infty} dq e^{-\alpha q^2/\tau} \int_{-\infty}^{\infty} dp e^{-\beta p^2/\tau} = \frac{1}{h} \frac{\pi \tau}{\sqrt{\alpha \beta}}$$

where the $1/h$ term appeared due to the heisenberg uncertainty $\Delta p \Delta q \approx h$. If this makes you feel uncomfortable, like it makes me feel uncomfortable, don't worry because the constants don't actually matter; because when we calculate the energy:

$$U = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau} \right) = \tau$$

everything vanishes! Note that since we had two quadratic degrees of freedom, that we had Z being proportional to τ . If instead we had say five quadratic degrees of freedom, we would have found Z proportional to $\tau^{5/2}$, and correspondingly we would have found U to be proportional to $5\tau/2$, since the power of τ comes through as a constant factor when you take the log. All this is to say that every additional quadratic degree of freedom adds $\tau/2$ to the energy of the system (where this is a system of a single particle).

Note that we can consider the heat capacity:

$$C_V = \frac{\partial U}{\partial T} = \frac{n}{2}$$

where n is the number of quadratic degrees of freedom. Note that in our calculations, we assumed that the thermal energy dominates the energy spacings for the degrees of freedom, which is not always true. For instance, up to $200K$, the thermal energy only dominates the energy spacings for the translational degrees of freedom for a diatomic molecule (so the heat capacity is $3/2$), then from $200K$ to $2000K$ the thermal energy dominates the translational degrees of freedom and two rotational degrees of freedom (so the heat capacity is $5/2$), then beyond $2000K$ the thermal energy also dominates two vibrational degrees of freedom for a diatomic molecule (so the heat capacity is $7/2$).