Physics 101B. Modern Physics. Professor Dine

Some Aspects of Statistical Mechanics

1 Derivation of the Ideal Gas Law

From the Boltzman distribution we can derive the ideal gas law. This is a good example of how features of a macroscopic system – the pressure, temperature, volume – are related to microscopic features of the system. Consider a gas in a container. We want to calculate the pressure on the walls. Take the wall to be in the yz plane. Then each time a particle with velocity (v_x, v_y, v_z) hits the wall, it's v_x changes sign, but v_y and v_z stay the same (we are assuming that the wall is not sticky, so particles just bounce off elastically). This means that the momentum *imparted to the wall* is $2mv_x$. Now the force on the wall is the momentum imparted per unit time. The force per unit area is the momentum imparted per unit time per unit area. For a given velocity, we need to multiply by the flux – the number of particles with that velocity per unit area incident on the surface per unit time. This is the density times v_x. Finally, e need to remember that there is a distribution of values of v_x. So we have to integrate over v_x with the probability function $f(v_x, v_y, v_z)$. So

$$P = \int_o^\infty dv_x \int_{-\infty}^\infty dv_y \int_{-\infty}^\infty dv_z f(\vec{v})(2v_x^2)\frac{N}{V} \tag{1}$$

The limits on the v_x integral are set by the fact that the velocity must be positive, corresponding (in my convention) to a particle incident on the wall (it doesn't matter if you take this to be a negative velocity). Because everything else in this expression is even in v_x, we can integrate over all velocities and divide by two. So the pressure is:

$$P = \frac{N}{V}\frac{\langle E \rangle}{m} = \frac{N}{V}kT. \tag{2}$$

This is the ideal gas law.

2 Some aspects of Quantum Statistics

Both the Fermi-Dirac and Bose-Einstein distributions go over to the Boltzman distribution if $e^\alpha \gg 1$. Each becomes:

$$e^{-\alpha}e^{-E/kT} \tag{3}$$

so, comparing with the Maxwell-Boltzmann distribution,

$$e^{-\alpha} = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2}. \tag{4}$$

Clearly this becomes better as the density becomes smaller and/or the temperature becomes larger.

We can derive an a priori condition for the validity of classical statistical mechanics: the typical separation of particles should be larger than their De Broglie wavelength. This is the condition:

$$\lambda = \frac{\hbar}{p} = \frac{\hbar}{(2mkT)^{1/2}} \tag{5}$$

With $d = \left(\frac{V}{N}\right)^{1/3}$, the typical separation, this is the condition:

$$\frac{\lambda}{d} \ll 1 \qquad \frac{N}{V}\left(\frac{2mkT}{\hbar}\right)^{-3/2} \ll 1. \tag{6}$$

3 Bose-Einstein Condensation

Consider a free Bose-gas, at very low temperatures. The Bose-Einstein distribution function is potentially singular because of the minus sign:

$$f(E) = \frac{1}{e^{\alpha + E/kT} - 1} \tag{7}$$

We must insist that $\alpha \geq 0$ if a probability interpretation is to hold. Suppose that $\alpha = 0$ at some temperature T_o. As for other problems we have encountered, summing over plane wave states, $\sum_{\vec{n}}$, we can replace the sum by an integral. This gives, for the total number of particles:

$$\frac{N}{V} = \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{e^{E(p)/kT} - 1}. \tag{8}$$

We can do this integral. $\int d^3p = 4\pi p^2 dp$. Also, $dE = p/mdp = \sqrt{2E/m}dp$. So

$$\frac{N}{V} = \frac{1}{2\pi^2\hbar^3}\int dE\sqrt{2m^3}\frac{E^{1/2}}{e^{E/kT_o} - 1}. \tag{9}$$

This is an equation for T_o. To determine it, call:

$$x = \frac{E}{kT_o}. \tag{10}$$

So

$$\frac{N}{V} = \frac{1}{4\pi^2}\left(\frac{2mkT_o}{\hbar^2}\right)\int_o^\infty dx \frac{x^{1/2}}{e^x - 1}. \tag{11}$$

This last integral you can look up; it is $\zeta(3/2)\Gamma(3/2)$. $\zeta(3/2) \approx 2.612$. $\Gamma(3/2) = 1/2\sqrt{\pi}$. When you plug in, for helium, one finds $T_c = 3.1^o$K. The real transition temperature is 2.17. This is pretty good, since the Helium atoms are interacting. Below this temperature, what is happening is that most of the particles are in the ground state. Calling $N = N_o$ plus an integral as before, one can show that as $T \rightarrow 0$, all of the particles are in the ground state.

4 Derivation of the Fermi-Dirac Distribution

Suppose we have energy levels with energy E_i, and each has degeneracy g_i. Suppose that overall we have N particles. We want to distribute them among the various levels. To distribute n_i particles among g_i states ($n_i < g_i$), there are:

$$\frac{g_i(g_i - 1)\ldots(g_i - n_i + 1)}{n_i!} = \frac{g_i!}{n_i!(g_i - n_i)!} \tag{12}$$

possibilities. So we need to minimize:

$$P = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \tag{13}$$

subject to the constraint that the total number of particles is fixed, as is the energy. As for the Boltzman distribution, we take the log, and add lagrange multipliers, α and β for the constraints. Then we minimize:

$$W = \ln(g_i!) - \ln(n_i!) - \ln(g_i - n_i)! + \alpha \sum n_i - N + \beta \sum (n_i E_i) - E. \quad (14)$$

Using Stirlings formula as before gives the equation:

$$(g_i - n_i) = n_i e^{\alpha + \beta E_i} \quad (15)$$

and solving for n_i:

$$n_i = \frac{g_i}{1 + e^{\alpha + \beta E_i}}. \quad (16)$$

It is not assigned, but if you are interested, you should work through the details of this derivation as an exercise. I would be happy to discuss this in office hours, and Jeff can explain it in section.