Physics 112 : Lecture 13

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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1 Finishing up the debye model

Recall from last lecture that we derived the heat capacity of a solid using the debye model in terms of the debye temperature, T_D. In the limit $T >> T_D$ we have $C_V = 3Nk$, and for the limit $T << T_D$ we have $C_V \approx T^3$. You might think that at ordinary temperatures, we only ever observe one of the two limits, but sadly no; the debye temperature for lead is $T_D = 105K$, but the debye temperature for diamond is $T_D = 2200K$, so at room temperature we see the high temperature limit for lead, and the low temperature limit for diamond.

If we wanted to *improve* our model, one thing we could do is incorporate different "speed of sounds" into our model, i.e. including the speed of sound for longitudinal waves, the speed of sound for transverse waves, and so on; which we assumed in our simple model were all equal. Our idea that all the modes are equal will no longer be true.

2 Chemical Potential

So far, we've been restricting ourselves to the case where there is no particle transfer between the systems in consideration. If we remove this restriction, we introduce a new variable known as the chemical potential M [1]. If we have two systems at chemical potentials M_1 and M_2, and $M_1 > M_2$, then we expect particles to flow from system 1 to system 2.

Now, consider a general case, where we have two systems S_1, S_2, which have respective volumes V_1, V_2, which are both connected to the same thermal reservoir at a temperature τ. We allow the two systems to exchange particles. We know that when a system is connected to a thermal reservoir at equilibrium, then *the helmholtz free energy must be minimized.* The free energy for this system is:

$$F = F_1 + F_2 = U_1 + U_2 - \tau(\sigma_1 + \sigma_2)$$

with conservation of particles $N = N_1 + N_2$ where N_1, N_2 are the number of particles of system 1 and system 2 respectively. Note that the change in the free energy is given:

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[1] this might be a μ, it's hard to tell

$$\delta F = \left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} \partial N_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2} \partial N_2 = 0$$

by the conservation of particles, we have $\partial N_1 = -\partial N_2$, so for equilibrium we have:

$$\left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} = \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2}$$

So now, we have found a good candidate for our 'chemical potential' defined earlier, we define:

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

since if we have two systems at equal chemical potential, by the above derivation, there is no exchange of particles. With this definition in hand, we can return to our earlier formula for the change in free energy, and find that:

$$\partial F = [M_1 - M_2] dN_1$$

So, if $M_1 > M_2$, and $dN_1 < 0$, then $dF < 0$, which means that if particles leave system 1 to system 2, the free energy of the system drops, which is required for equilibrium. As a small side note, in our definition for chemical potential we took a derivative with respect to the number of particles, but numbers are discrete! So more correctly, we have:

$$M(\tau, V, N) = F(\tau, V, N) - F(\tau, V, N-1)$$

but they should be approximately the same. When you have multiple species inside the same system (i.e. maybe carbon, oxygen, argon, ...) you need to consider the chemical potentials of each of the species. Now, we will derive the chemical potential for a single ideal gas. We know that for an ideal gas:

$$F = -\tau \ln Z; \qquad Z = \frac{Z_1^N}{N!}; \qquad Z_1 = n_Q V$$

where Z_1 is the partition function for a single gas atom. So we have free energy:

$$F = -\tau[N \ln Z_1 - \ln N!]$$

$$M = F(N) - F(N-1) = -\tau[\ln Z_1 - \ln N] = \tau \ln\left(\frac{n}{n_Q}\right)$$

where n is the density N/V, and n_Q is the quantum concentration constant defined in a previous lecture. So, as expected, in a system with high density, we have high chemical potential, so particles will flow to a system with low density, with a low chemical potential.

Additionally, if we wanted, we could apply a potential difference to the two systems S_1 and S_2 (maybe by applying a voltage). The new effective total chemical potential is:

$$M_{\text{total}} = M_{\text{internal}} + M_{\text{external}}$$

where the M_{internal} was what we already described, and M_{external} is the external potential applied. As a toy example, we can consider the atmosphere:

$$M = \tau \ln(n/n_Q) + mgh$$

and if we equate the chemical potential of the atmosphere at height h, and at height 0 (because the atmosphere is approximately in equilirbium), then we find that:

$$n(h) = n(0)e^{-mgh/\tau}$$