PHYC - 505: Statistical Mechanics Homework Assignment 2 Solutions

Due February 11, 2014

1. Work out fully an expression for the Debye specific heat for a 1-dimensional solid at temperature T. Show all your steps so it will be clear you have understood the Debye derivation. Show what limits the expression you get has at high and low temperatures. What does high and low mean here precisely?

In the Debye model, the atoms in the lattice are interacting with each other. These interactions cause the existence of quantized lattice vibrations, known as phonons. Let us consider a simple model for these interactions. Suppose we have a 1-d ring of N particles, each of mass, m, and coupled to its nearest neighbors with spring forces as in the figure below.



The equation of motion of the n^{th} particle is

$$m\ddot{x}_n = -k(x_n - x_{n+1} + x_n - x_{n-1})$$

$$\ddot{x}_n = -\omega_0^2 (2x_n - x_{n+1} - x_{n-1})$$

where ω_0 is the natural frequency of the coupling. Here it is necessary to change the space from one in which the particles are interacting (*n*-space) to one in which they are not (*q*-space). The equations of motion can be decoupled by performing a discrete Fourier transform defined as

$$x^q \equiv \sum_n e^{iqn} x_n$$

Applying this transform we have

$$\sum_{n} e^{iqn} \left(\ddot{x}_{n} = -\omega_{0}^{2} \left(2x_{n} - x_{n+1} - x_{n-1} \right) \right)$$
$$\ddot{x}^{q} = -\omega^{2} \left(2x^{q} - e^{-iq} \sum_{n} e^{iq(n+1)} x_{n+1} - e^{iq} \sum_{n} e^{iq(n-1)} x_{n-1} \right)$$
$$= -\omega^{2} \left(2x^{q} - e^{-iq} \sum_{\alpha} e^{iq\alpha} x_{\alpha} - e^{iq} \sum_{\beta} e^{iq\beta} x_{\beta} \right)$$
$$= -\omega^{2} \left(2x^{q} - e^{-iq} x^{q} - e^{iq} x^{q} \right)$$
$$= -\omega^{2} x^{q} \left(2 - 2\cos(q) \right)$$
$$= -4\omega^{2} x^{q} \sin\left(\frac{q}{2}\right)$$
$$= -\omega_{q}^{2} x^{q}$$

where

$$\omega_q = 2\omega_0 \left| \sin\left(\frac{q}{2}\right) \right|$$

This q-space equation of motion takes on the form of a simple harmonic oscillator with frequency ω_q . This is the q^{th} normal mode.

Notice that, for a ring of N spring-connected masses, the periodic boundary conditions are such that

$$e^{iqn} = e^{iq(n+N)}$$

From this it is seen that the allowed values of q can be calculated as

$$e^{iqn} = e^{iqn}e^{iqN}$$
$$1 = e^{iqN}$$
$$q = \frac{2\pi}{N}\nu$$

where ν takes on integer values between 0 and N-1, inclusively, and so q takes on the values from 0 to 2π . Thus we have converted N coupled oscillators in n-space into N decoupled oscillators in q-space. The price we pay is that each oscillator oscillates at a different frequency. The partition function for a single mode with frequency ω_q is calculated (using the fact that the energy of a quantum harmonic oscillator, with frequency ω_q , is $E_n = \left(n + \frac{1}{2}\right) \hbar \omega_q$ as follows

$$\begin{aligned} \mathcal{Z} &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_q \left(n + \frac{1}{2}\right)} \\ &= e^{-\beta \hbar \omega_q / 2} \sum_{n=0}^{\infty} \left(e^{-\beta \hbar \omega_q}\right)^n \\ &= \frac{e^{-\beta \hbar \omega_q / 2}}{1 - e^{-\beta \hbar \omega_q}} \end{aligned}$$

and the average energy for this single mode can be found as

$$\begin{split} \langle E \rangle &= -\frac{\partial}{\partial\beta} \ln \mathcal{Z} \\ &= -\frac{\partial}{\partial\beta} \left(-\beta \frac{\hbar\omega_q}{2} - \ln\left(1 - e^{-\beta\hbar\omega_q}\right) \right) \\ &= \frac{\hbar\omega_q}{2} + \frac{\hbar\omega_q e^{-\beta\hbar\omega_q}}{1 - e^{-\beta\hbar\omega_q}} \\ &= \frac{\hbar\omega_q}{2} + \frac{\hbar\omega_q}{e^{\beta\hbar\omega_q} - 1} \end{split}$$

(Note that, without the ground state energy, $\frac{\hbar\omega_q}{2}$, there is a resemblance to Bose-Einstein statistics.) The average energy for the entire 1-d solid would then be found by summing over all the modes in q-space as

$$\langle E \rangle = \sum_{q \text{ modes}} \left(\frac{\hbar \omega_q}{2} + \frac{\hbar \omega_q}{\mathrm{e}^{\beta \hbar \omega_q} - 1} \right)$$

Ignoring the ground state energy we have

$$\langle E \rangle = \sum_{q \text{ modes}} \frac{\hbar \omega_q}{\mathrm{e}^{\beta \hbar \omega_q} - 1}$$

If we approximate N >> 1, we can convert this sum over the q-modes into an integral with respect to q as follows: first we multiply by 1, that is, $\Delta \nu = 1$, since ν is an integer between 0 and N - 1.

$$\begin{split} \langle E \rangle &= \sum_{q \text{ modes}} \frac{\hbar \omega_q}{\mathrm{e}^{\beta \hbar \omega_q} - 1} \Delta \nu \\ &= \sum_{q \text{ modes}} \frac{\hbar \omega_q}{\mathrm{e}^{\beta \hbar \omega_q} - 1} \Delta \left(\frac{N}{2\pi} q \right) \\ &= \frac{N}{2\pi} \sum_{q \text{ modes}} \frac{\hbar \omega_q}{\mathrm{e}^{\beta \hbar \omega_q} - 1} \Delta q \\ &\approx \frac{N}{2\pi} \int_0^{2\pi} \frac{\hbar \omega_q}{\mathrm{e}^{\beta \hbar \omega_q} - 1} dq \end{split}$$

Next we notice that for small q,

$$\omega_q = 2\omega_0 \left| \sin\left(\frac{q}{2}\right) \right| \to \omega_0 q$$

We will therefore approximate the dispersion relation to be

$$\omega_q \approx \omega_0 q$$

and can be rewritten in terms of c_s is the speed of sound in the medium and a is the interatomic spacing as

$$\omega_q = \frac{c_s}{a}q$$

Note: This is a good approximation for small q (acoustic phonons), but rather bad for large q. This yields a differential

$$d\omega_q = \omega_0 dq$$

Combining these two approximations, we have that the average energy can be rewritten as

$$\begin{split} \langle E \rangle &\approx \frac{N}{2\pi} \int_0^{2\pi\omega_0} \frac{\hbar\omega_q}{\mathrm{e}^{\beta\hbar\omega_q} - 1} \frac{d\omega_q}{\omega_0} \\ &= \frac{N}{2\pi\omega_0} \int_0^{\omega_{\max}} \frac{\hbar\omega_q}{\mathrm{e}^{\beta\hbar\omega_q} - 1} d\omega_q \end{split}$$

This is typically rewritten by introducing the Debye temperature, T_D , defined by the relation

 $k_B T_D = \hbar \omega_{\rm max} = 2\pi \omega_0$

Changing the integration variables above to dimensionless ones, $x = \beta \hbar \omega_q$, we have

$$\begin{split} \langle E \rangle &= \frac{N}{2\pi\omega_0} \int_0^{\omega_{\max}} \frac{\hbar\omega_q}{\mathrm{e}^{\beta\hbar\omega_q} - 1} d\omega_q \\ &= \frac{N}{2\pi\omega_0} \int_0^{\beta\hbar\omega_{\max}} \frac{1}{\beta} \frac{\beta\hbar\omega_q}{\mathrm{e}^{\beta\hbar\omega_q} - 1} \frac{d\left(\beta\hbar\omega_q\right)}{\beta\hbar} \\ &= \frac{N}{2\pi\omega_0} \frac{1}{\beta^2\hbar} \int_0^{T_D/T} \frac{x}{\mathrm{e}^x - 1} dx \\ &= \frac{Nk_BT^2}{T_D} \int_0^{T_D/T} \frac{x}{\mathrm{e}^x - 1} dx \end{split}$$

Unfortunately, this integral cannot be evaluated in terms of elementary functions (although an expression exists in terms of special functions), but we can look at some limiting cases. When the temperature is much greater than the Debye temperature x in the integrand is always small so we can make the approximation

$$e^x \approx 1 + x$$

so we have that the average energy for $T >> \frac{2\pi\hbar\omega_0}{k_B}$ is

$$\begin{split} \langle E \rangle &= \frac{Nk_B T^2}{T_D} \int_0^{T_D/T} \frac{x}{\mathrm{e}^x - 1} dx \\ &\approx \frac{Nk_B T^2}{T_D} \int_0^{T_D/T} \frac{x}{1 + x - 1} dx \\ &= \frac{Nk_B T^2}{T_D} \int_0^{T_D/T} \frac{x}{x} dx \\ &= \frac{Nk_B T^2}{T_D} \int_0^{T_D/T} dx \\ &= \frac{Nk_B T^2}{T_D} \frac{T_D}{T} \\ &= Nk_B T \end{split}$$

and the heat capacity at constant volume of this limit is then found by taking the temperature derivative of the average energy as

$$C_V = \frac{d\langle E \rangle}{dT} = Nk$$

in the high temperature limit.

On the other hand, in the limit that the temperature is much smaller than the Debye temperature, that is, $T << \frac{2\pi \hbar \omega_0}{k_B}$, the upper limit can be replaced by infinity without much loss of accuracy due to the fact that the integrand goes like e^x for large x. When the integral is extended to infinity, it can be calculated analytically in terms of the Riemann zeta and gamma functions as

$$\begin{split} \langle E \rangle &= \frac{Nk_B T^2}{T_D} \int_0^{T_D/T} \frac{x}{\mathrm{e}^x - 1} dx \\ &\approx \frac{Nk_B T^2}{T_D} \zeta(2) \Gamma(2) \\ &= \frac{\pi^2}{6} \frac{Nk_B T^2}{T_D} \end{split}$$

and the heat capacity at constant volume becomes

$$C_V = \frac{\pi^2}{3} N k_B \frac{T}{T_D}$$

Notice that this is proportional to T since we are in one dimension instead of T^3 as in the three dimensional case.

2. Calculate the energy density of states for a 2-dimensional system that is otherwise similar to a free electron of mass m confined to a square of side L but is different in that the energy momentum relationship is $E = Gp^3$ rather than $E \sim p^2$, G being a constant of appropriate dimensions. Calculate the (temperature dependence of the) specific heat of a collection of N such noninteracting electrons in thermal equilibrium at temperature T.



Consider the Hamiltonian

$$H = Gp^3$$

In the semi-classical limit, the partition function for one particle in such a system, accounting for the spin, can be calculated as follows

$$\mathcal{Z}_1 = \frac{2}{h^2} \int d^2 x \int d^2 p e^{-\beta E}$$
$$= \frac{2}{h^2} \int_0^L dx \int_0^L dy \int d^2 p e^{-\beta G p^3}$$
$$= \frac{2L^2}{h^2} \int d^2 p e^{-\beta G p^3}$$

Now considering a circle of radius p, the above integral becomes

$$\mathcal{Z}_1 = \frac{2L^2}{h^2} \int_0^\infty 2\pi p dp \mathrm{e}^{-\beta G p^3}$$
$$= \frac{4\pi L^2}{h^2} \int_0^\infty p dp \mathrm{e}^{-\beta G p^3}$$

see http://en.wikipedia.org/wiki/N-sphere. Now using the substitution that

$$E = Gp^3 \quad \rightarrow \quad p = \left(\frac{E}{G}\right)^{1/3} \quad dE = 3Gp^2dp = 3G^{1/3}E^{2/3}dp$$

we have that

$$\begin{aligned} \mathcal{Z}_1 &= \frac{4\pi L^2}{h^2} \int_0^\infty p dp \mathrm{e}^{-\beta G p^3} \\ &= \frac{4\pi L^2}{h^2} \int_0^\infty \left(\frac{E}{G}\right)^{1/3} \frac{1}{3G^{1/3} E^{2/3}} dE \mathrm{e}^{-\beta E} \\ &= \frac{4\pi L^2}{3h^2 G^{2/3}} \int_0^\infty \mathrm{e}^{-\beta E} E^{-1/3} dE \end{aligned}$$

Here we see that this takes on the form

$$\mathcal{Z} = \int_0^\infty g(E) \mathrm{e}^{-\beta E} dE$$

where g(E) is the energy density of states, and so we have that the density of states is

$$g(E) = \frac{4\pi L^2}{3h^2 G^{2/3}} E^{-1/3}$$

Now, in order to calculate the heat capacity, we find the average energy of the system, by first finding the partition function of the system as follows

$$\begin{split} \mathcal{Z} &= \frac{Z_1^N}{N!} \\ &= \frac{1}{N!} \left(\frac{4\pi L^2}{3h^2 G^{2/3}} \int_0^\infty e^{-\beta E} E^{-1/3} dE \right)^N \\ &= \frac{1}{N!} \left(\frac{4\pi L^2}{3h^2 G^{2/3}} \beta^{-2/3} \int_0^\infty e^{-\beta E} (\beta E)^{-1/3} d(\beta E) \right)^N \\ &= \frac{1}{N!} \left(\frac{4\pi L^2}{3h^2 G^{2/3}} \beta^{-2/3} \int_0^\infty e^{-x} x^{-1/3} dx \right)^N \\ &= \frac{1}{N!} \left(\frac{4\pi L^2}{3h^2 G^{2/3}} \beta^{-2/3} \Gamma \left(\frac{2}{3} \right) \right)^N \end{split}$$

The average energy is then found as

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln \mathcal{Z} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial\beta}$$

$$= -\frac{N!}{\left(\frac{4\pi L^2}{3h^2 G^{2/3}}\beta^{-2/3}\Gamma\left(\frac{2}{3}\right)\right)^N} \frac{1}{N!} \left(\frac{4\pi L^2}{3h^2 G^{2/3}}\Gamma\left(\frac{2}{3}\right)\right)^N \left(-\frac{2N}{3}\beta^{-2N/3-1}\right)$$

$$= \frac{2}{3}N\beta^{-1}$$

$$= \frac{2}{3}Nk_BT$$

and the heat capacity at constant volume is

$$C_V = \frac{2}{3}Nk_B$$

According to the 1st law of the thermodynamics dU=Q-W= Q-PJV. Here I assume the nork done on or by the system is the PV work. By means of the relation between & and S (entropy), we obtain JU=TJS-PJV-To find the connections to other themadynamic potentials, we Could rewrite Pdv = d(Pv) - VdP, Then, it Sallows that dU=-dPV+VdP+Tds (U+PV) = dF1 = TJS + VJP. where H is as known as the enthapy. If we write TJS = d(TS)-SdT, the followholds free energy is obtained $d(V-TS) \equiv dF = -SdT - PdV$ The Gibs free energy is dF=-SdT-dPV+Vdp $= \int J(F+PV) = -SJT+VJP /$