

1. In this problem, we will try and understand a phonon gas and its fluctuations. This model can also be extended to the vibrations of atoms in a cold solid.

- (a) First, a refresher: derive the relationship between  $\langle E \rangle$  and  $\langle (\delta E)^2 \rangle$  in the canonical ensemble. Also, show that  $\langle (\delta E)^2 \rangle = \frac{\partial^2 \ln Q}{\partial \beta^2}$ .
- (b) The energies of a harmonic oscillator are given by  $E_n = (n+1/2)\hbar\omega$ ,  $n = 0, 1, 2, \dots$ . Calculate the partition function  $q$  associated with this system, again in the canonical ensemble. Hint: you can use a geometric series to simplify this sum.
- (c) Now let's imagine a collection of  $N$  such harmonic oscillators vibrating in  $D$  dimensions forming the system. Since multiple harmonic oscillators can occupy the same energy state, the energy of the system is now given by

$$E_\nu = E_0 + \sum_{\alpha=0}^{DN} n_\alpha \hbar\omega_\alpha \text{ where } E_0 \equiv \sum_{\alpha=0}^{DN} \frac{1}{2} \hbar\omega_\alpha$$

$E_0$  is the just ground state energy of the full system. Find the canonical partition function of this system by summing over all the possible states of each oscillator:

$$Q(\beta, N, V) = \sum_{n_1, n_2, \dots = 0}^{\infty} \exp \left[ -\beta \sum_{\alpha} \left( \frac{1}{2} + n_{\alpha} \right) \hbar\omega_{\alpha} \right]$$

You should find (using your  $q$  for one particle from (b)) that your answer should be:

$$\ln Q = - \sum_{\alpha=0}^{DN} \ln [\exp(\beta \hbar\omega_{\alpha}/2) - \exp(-\beta \hbar\omega_{\alpha}/2)]$$

Hint: since each exponential factor of  $n_{\alpha}$  is independent, this expression can be simplified to a product of partition functions.

- (d) Find the average energy of this system using your relations from part (a).
- (e) Again, let's remind ourselves of some connections between statistical mechanics and thermodynamics. Let's find the relationship between the canonical partition function and the Helmholtz free energy.

You can do this by using the Gibbs' definition of entropy from Problem Set 1 ( $S = -k_B \sum_{\nu} P_{\nu} \ln P_{\nu}$ ) and plugging in the probability distribution of microstates in the canonical ensemble. Further simplify this expression and remember that  $A = E - TS$  in order to obtain  $A = -k_B T \ln Q$ .

- (f) Now that you have  $Q$  for the phonon gas, you can obtain the Helmholtz free energy by integrating over frequencies of the phonons. Assume that you have a frequency spectrum that looks like  $g(\omega)d\omega = \delta(\omega - \omega_0)$ . Here,  $g(\omega)d\omega$  gives the number of phonon states with frequency between  $\omega$  and  $\omega + d\omega$ . If it is a delta function, only one phonon level is populated (a reasonable picture at low temperatures).

2. Now we will look more closely at the grand canonical partition function for a single component open system and relate it to different thermodynamical properties.

- (a) Start by writing down the Gibb's entropy and plugging in the grand canonical probability distribution. Show that this becomes  $S = k_B\beta\langle E \rangle - k_B\beta\mu\langle N \rangle + k_B \ln Z$ .
- (b) We know that  $dE = TdS - pdV + \mu dN$ . Using the fact that some thermodynamic quantities are extensive while some are intensive as well as the properties of homogeneous functions, one can show that  $E = TS - pV + \mu N$  (you don't have to prove this now since we'll do it later in the course). Using this, do a Legendre transform to find an expression for a new function  $\Phi \equiv E - TS - \mu N$ .
- (c) Now relate your answers from parts (a) and (b) to find how  $Z$  and  $\Phi$  are related to each other. You should be able to find that  $\ln Z = -\beta\Phi$ .
- (d) Let's see how the derivatives of  $Z$  give us more information about the properties of our system. First, we will try to find the energy. Write down an expression for the average energy as a sum in terms of probabilities. You should be able to relate this expression to a derivative of  $\ln Z$  with respect to  $-\beta$ . Notice what's held constant in this derivative and how it is different from what we found previously for the canonical ensemble.
- (e) We can also find the other quantity that fluctuates in an open system,  $\langle N \rangle$ , from the partition function. Write an expression for  $\langle N \rangle$  as a sum using probabilities of microstates in the grand canonical ensemble. You should notice that this can also be obtained from an appropriate derivative of  $\ln Z$ , similar to  $\langle E \rangle$ .
- (f) This is not a question, but something to think about. Notice that the averages are related to what you take the derivative of  $\ln Z$  with respect to. For example,  $\langle E \rangle$  is obtained from a derivative with respect to  $-\beta$ , which is what appears in front of  $E_\nu$  in the expression for  $P_\nu$  or  $Z$ . Similarly, notice the pattern for  $\langle N \rangle$ . This is a helpful key to understand what derivatives to take of the partition function for any ensemble to get the appropriate average thermodynamic quantity.
- (g) Relate  $\langle (\delta N)^2 \rangle$  to the appropriate derivative of  $\langle N \rangle$  and the appropriate second derivative of  $\ln Z$ .