PHY 831: Statistical Mechanics
Homework 2

Due Monday September 27th, 2021

1. Show that
$$\left(\frac{\partial E}{\partial N}\right)_{T,V} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V}.$$

2. Prove the relationship
$$C_P = C_V + TV\frac{\alpha_P^2}{\kappa_T},$$
where the expansivity $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$ and the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$. Since the isothermal compressibility is always greater than zero for a thermodynamically stable gas, this implies the heat capacity at constant pressure is always greater than the heat capacity at constant volume. Explain in very simple terms why $C_P > C_V$ makes physical sense.

3. Assume that the entropy S and the multiplicity factor Ω for some physical system are related through an arbitrary functional form,
$$S = f(\Omega).$$
Show that the additive feature of S and the multiplicative character of Ω necessarily require that $f(\Omega) = k\log\Omega$, where k is some constant. Hint: consider the derivatives of $f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2)$.

4. An "Einstein solid" is a simple model of a solid that makes use of the fact that each atom can oscillate about it's equilibrium lattice site, and therefore treats the system as N independent harmonic oscillators, all with the same frequency ω [1].

   (a) Derive the multiplicity function $\Omega(N, q)$ for a system of N harmonic oscillators with total energy $E = q\hbar\omega = \sum_{i=1}^{N} n_i\hbar\omega$. Hint: This is the same combinatoric problem as finding the number of different ways to arrange q balls in N urns. Moreover, this is a commonly worked out example in many text books :).

   (b) For the limit where $N >> 1$ use Stirling's approximation to derive the asymptotic form for the entropy as a function of N, q, and use this to show that the total energy E at temperature T is
$$E = \frac{N\hbar\omega}{\exp(\hbar\omega/k_BT) - 1}.$$

[1] Actually, since each atom can vibrate in 3-independent directions, you would model it as $3N$ oscillators. Here we don't worry about this detail.

This is the famous result of Max Planck. Later, we'll derive this in a more modern and less cumbersome way using partition functions, etc., that steer clear of having to find multiplicity functions.

5. Consider two thermally isolated Einstein solids each consisting of $N_A = N_B = 3$ oscillators. Initially, the two solids are separated with an adiabatic wall, with $q_A = 0$ and $q_B = 6$, which is subsequently removed so that they can exchange heat. Make a table with columns labelled q_A, Ω_A, q_B, Ω_B, and $\Omega = \Omega_A\Omega_B$, and enumerate all possibilities that the system can relax to. What are the most likely new equilibrium values for q_A and q_B ?

6. Now consider two Einstein solids with $N_A = 300$, $N_B = 200$ and $q = q_A + q_B = 100$. Use a computer (Excel spreadsheet, a simple Python code, Mathematica, or whatever else you're comfortable with) to make a similar table as the previous problem for the possible 101 macrostates, and make a plot of the total multiplicity function $\Omega_A\Omega_B$ as a function of q_A.