PHY 831: Statistical Mechanics
Homework 3

Due Monday Oct 4, 2021

1. The 1^{st} Law for a 1-dimensional system (e.g., a stretched wire, spring, polymer, etc.) reads
$$dE = TdS + f dl \,,$$
where f is the external force and dl is the change in length. (Note that the sign of the differential work term differs from the more familiar $-PdV$ because pressure is defined as the outward force on the container.) Let us consider a polymer chain of N links each of length ρ, with each link equally likely to be directed to the right and left.

   (a) We can recycle our previous work on the multiplicity function for a paramagnet $\Omega(N, s)$ to describe this system. Argue that the number of arrangements (i.e., microstates) that give a head-to-tail length of $l = 2|s|\rho$ (i.e., macrostate) is equal to
$$\Omega(N, s) + \Omega(N, -s) = \frac{2N!}{(N/2 + s)!(N/2 - s)!}$$

   (b) For $|s| << N$, show that (working in natural units with $k_B = 1$)
$$S = \log\bigl(2\Omega(N, 0)\bigr) - \frac{l^2}{2N\rho^2} \,.$$

   (c) What is the force f at extension l? This force arises because the polymer wants to coil up (entropy is higher in a coiled configuration than when it's straight.). For instance, if you heat up a rubber band, it contracts.

2. Consider a system of N independent quantum harmonic oscillators at constant T with angular frequency ω.

   (a) Compute i) partition function, ii) the average energy, iii) the Helmholtz free energy, and iv) the heat capacity C_V for a single oscillator.

   (b) Now compute the partition function and average energy for a *c*lassical oscillator. In what limit does $\langle E \rangle$ become equal to the result from the quantum calculation?

   (c) Show in general that if you have two non-interacting subsystems in thermal equilibrium (i.e., at the same fixed termperature), the partition function factorizes $Z(1 + 2) = Z(1)Z(2)$.

(d) Compute the same quantities as in part a), but now for the system of N oscillators.

3. Consider an ideal gas of N identical O_2 molecules, where all molecules have total spin $S = 1$. The gas is in a uniform magnetic field in the z-direction, so the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} - \mu B S_i^z \right) .$$

(a) Treating the spatial degrees of freedom classically but the spin degrees of freedom as quantized, calculate the partition function $Z(T, N, V, B)$.

(b) What are the probabilities for a given molecule to have S_z values of $-1, 0, 1$ at temperature T?

(c) Compute the average magnetization per volume $\langle M \rangle / V$, where $M = \mu \sum_i S_i^z$.

(d) Compute the zero-field isothermal susceptibility $\chi_T = \frac{\partial \langle M \rangle}{\partial B}\Big|_{B=0}$

4. Consider a rod-shaped molecule with moment of inertia I and electric dipole moment μ. In a uniform electric field $\mathcal{E}$ in the z-direction, there will be rotational motion governed by the Hamiltonian

$$\mathcal{H}_{\mathrm{rot}} = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu \mathcal{E} \cos \theta \, .$$

The molecule is connected to a heat bath, so is at constant temperature T.

(a) What is the (classical) partition function due to the rotational degrees of freedom?

(b) What is the average polarization $P = \langle \mu \cos \theta \rangle$?

(c) Compute the zero-field isothermal polarizability $\chi_T = \frac{\partial P}{\partial \mathcal{E}}\Big|_{\mathcal{E}=0}$

(d) Compute the average rotational energy and examine the low and high temperature limits.