Statistical Mechanics

September 24, 2008

Work 2 of the 3 problems. Please put each problem solution on a separate sheet of paper and put your name on each sheet.

Problem 1

An important quantity in statistical mechanics is the partition function Z. This function can be defined for any ensemble. Here you will use the partition function to derive a fundamental relationship in statistical mechanics and use this result to make the connection between theory and experiment:

$$Z(P,T,N) \propto \int d^{3N}q_i \, d^{3N}p_i \exp(-\beta H) \exp(\gamma P)$$

where $\beta = 1/k_B T$, H is the total energy of the system, and P is the pressure. As usual, the integration extends over all generalized particle coordinates q_i and particle momenta p_i. Assume the system contains N particles.

a. Determine γ such that $Z(P,T,N)$ is a partition function that belongs to the (P,T,N) ensemble. Hint: $G(P,T,N) = -\ln(Z)/\beta$. *(2 points)*

b. Show the following relationship holds in the (P,T,N) ensemble:

$$\sigma_V^2 \equiv \langle V^2 \rangle - \langle V \rangle^2 = -k_B T \left. \frac{\partial \langle V \rangle}{\partial P} \right|_{T,N}$$

(4 points)

c. This seems to be inconsistent: The fluctuations, σ_V^2, are always positive, yet there is a minus sign on the right hand side. How can you resolve this apparent contradiction? *(2 points)*

d. Comment on the significance of this formula in the context of the development of statistical mechanics in relation to laboratory experiments. Hint: Consider $\sigma_V/\langle V \rangle \equiv \sqrt{\langle V^2 \rangle - \langle V \rangle^2}/\langle V \rangle$ together with the observation that V scales linearly with the particle number N. *(2 points)*

Problem 2

Consider a system with energy levels labeled by $n = 0, 1, 2, 3, \ldots$ with energies

$$E_n = \mu_B H(2n + 1) \ ,$$

where each energy level has the degeneracy $N_n = AH$ (independent of n), namely the number of states at level n is N_n. Here, H is a uniform magnetic field and A is a positive number independent of H.

a. Compute the partition function

$$Z = \sum_{states} \exp(-energy/kT) \ .$$

Note that $Z \equiv Z(T, H)$, and the free energy is $F(T, H) = -kT \ln Z(T, H)$.

b. Compute the magnetization defined by

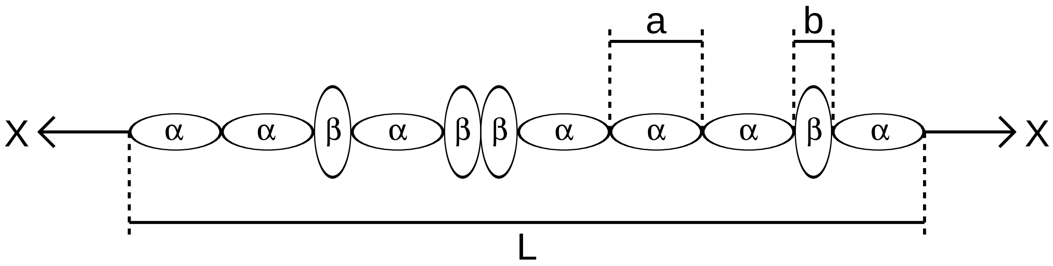
$$M(T, H) = -\frac{\partial F(T, H)}{\partial H} \ .$$

c. Is the system paramagnetic, diamagnetic, or ferromagnetic? The answer may depend on temperature. For temperatures at which it is paramagnetic or diamagnetic, compute the magnetic susceptibility

$$\chi_m = \left.\frac{\partial M(T, H)}{\partial H}\right|_{H=0} \ .$$

Problem 3

N monomeric units are arranged along a straight line to form a chain molecule. Each monomeric unit is assumed to be capable of being either in an α state or in a β state. In the former state, the length of a unit is a and its energy is E_α. The corresponding values in the latter case are b and E_β (see figure). Derive the relation between the length L of the chain molecule and the tension X applied between both ends of the molecule. Use the canonical ensemble at constant tension.



Hint: One may take advantage of the general canonical distribution by associating with each monomeric unit an energy $E_\alpha - aX$ or $E_\beta - bX$ depending on whether the unit is in the α or the β state.