Statistical Mechanics

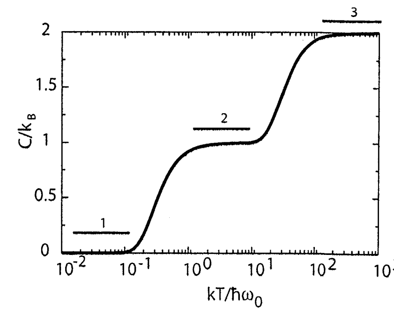
[35 pts] 1. A small molecule attached to the surface of a membrane in solution has two independent vibrational modes with very different spring constants. Classically, the potential can be written as

$$U(x_1, x_2) = \frac{1}{2}k_1 x_1^2 + \frac{1}{2}k_2 x_2^2 \qquad \text{with} \qquad k_2 = 100k_1. \tag{1}$$

(a) Give a relation between the spring constant k_1 and measured values for the thermal fluctuations $\langle x_1^2 \rangle$ at equilibrium with temperature T.

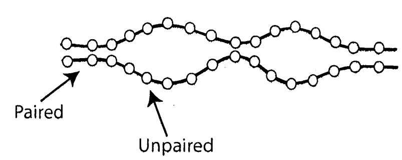
(b) For a given spring constant k_1, do the fluctuations $\langle x_1^2 \rangle$ depend in any way on properties of the solution (viscosity, density, etc.)? Explain.

(c) A measurement of the specific heat of the molecule as function of temperature is shown to the right. Explain the discrepancy from the classical result $C = 2k_\mathrm{B}$ (i.e., independent of temperature). In particular, interpret the three temperature ranges indicated by the labels 1–3.



[35 pts] 2. A simple model of double stranded DNA consists of the pairing of two strands with N links. Each link may or may not be bound to its partner on the other strand. Furthermore, an unpaired link can be in one of g states, while a paired link has a single conformation. So, each link can have energy

$$\epsilon_i = \begin{cases} \epsilon_0 < 0 & \text{with degeneracy } 1, \quad \text{paired} \\ 0 & \text{with degeneracy } g, \quad \text{unpaired} \end{cases} \tag{2}$$



(a) Show that the canonical partition function can be written as $Z = (g + \lambda)^N$ with $\lambda = e^{-\beta\epsilon_0}$ and $\beta = 1/k_\mathrm{B}T$.

(b) Find the fraction of paired links $f = \langle n \rangle / N$ as a function of temperature.

(c) At very low temperatures, nearly all the links are paired ($f \approx 1$). As T increases, the number of paired links decreases, reaching $f = 1/2$ at some temperature $T_{1/2}$. How does $T_{1/2}$ qualitatively depend on the degeneracy of the unpaired links? That is, if g increases, does $T_{1/2}$ increase or decrease? (No calculation is necessary, but explain your answer).

[**30 pts**] 3. In this question, we consider how the equation of state of a gas imposes restrictions on the form of thermodynamic quantities. In all parts of this problem, the notation reflects that the number of particles N is assumed to be constant.

(a) First, prove the Maxwell relation

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V . \tag{3}$$

which will be useful in parts (b) and (c).

(b) Show that the equation of state for an ideal gas

$$PV = Nk_{\mathrm{B}}T \tag{4}$$

implies that the energy is a function of temperature only. Use the following approach:

Starting from the relationship $\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$, show that $\left.\frac{\mathrm{d}E}{\mathrm{d}V}\right|_T = 0$ for an ideal gas. This means that $E(V,T) = E(T)$.

(c) Now consider a non-ideal gas that satisfies the van der Waals equation of state

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_{\mathrm{B}}T \tag{5}$$

where a and b are constants. Show that the constant volume specific heat of a van der Waals gas, C_V, depends only on temperature. That is, show that $\left.\frac{\mathrm{d}C_V}{\mathrm{d}V}\right|_T = 0$, which means that $C_V(V,T) = C_V(T)$.