

Problem 1A. (40 pts)

Consider a system of N molecules, each having energy levels $\epsilon_i = i\epsilon$ (where $i = 0, 1, 2, \dots$). (A system with equidistant energy levels).

- (1) Derive an expression for the partition function for this system.
- (2) At what temperature will the mean energy per molecule equal $\alpha\epsilon$ (α is just a number)?
- (3) Calculate the molecular partition function for the system at this temperature.
- (4) Calculate the entropy of the system at this temperature.

Perform these calculations for the general case of α and ϵ , and then evaluate these functions in the case when $\alpha = 1$ and $\epsilon = 3 \cdot 10^{-21}$ J.

(1) $q = 1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + e^{-3\epsilon/kT} + \dots = 1/(1 - e^{-\epsilon/kT})$ (recall the summation rule for geometrical series!);

$$Q = q^N = 1/(1 - e^{-\epsilon/kT})^N;$$

(2) The mean energy per molecule is $E/N = kT^2 \left(\frac{\partial}{\partial T} \ln q \right)_V = kT^2 \frac{\partial}{\partial T} \left(\ln \frac{1}{1 - e^{-\epsilon/kT}} \right) = \frac{\epsilon e^{-\epsilon/kT}}{1 - e^{-\epsilon/kT}}$

The condition $E/N = \alpha\epsilon$ then gives $\frac{e^{-\epsilon/kT}}{1 - e^{-\epsilon/kT}} = \alpha$, which can be rewritten as $e^{\epsilon/kT} - 1 = 1/\alpha$ and

then solved to give $T = \frac{\epsilon}{k \ln \left(1 + \frac{1}{\alpha} \right)}$.

(3) Substituting $e^{\epsilon/kT} = 1 + 1/\alpha$ into the above equation for q gives $q = 1 + \alpha$;

(4)

$$S = NkT \left(\frac{\partial}{\partial T} \ln q \right)_V + Nk \ln q = \frac{E}{T} + Nk \ln q = Nk\alpha \ln \left(1 + \frac{1}{\alpha} \right) + Nk \ln(1 + \alpha) = Nk[(1 + \alpha)\ln(1 + \alpha) - \alpha \ln \alpha]$$

The answers for $\alpha = 1$ and $\epsilon = 3 \cdot 10^{-21}$ J are: $T = \epsilon/(k \ln 2) = 313.6$ °K; $q = 2$; $S = 2 N k \ln 2$.

Problem 1B. (40 pts)

Consider a system of N particles, each having two energy levels (with energies 0 and ϵ); these particles are also known as two-level systems.

- (1) Derive an expression for the partition function for this system.
- (2) Calculate the total energy of this system.
- (3) Calculate the entropy of this system.
- (4) Calculate the heat capacity C_v of this system.
- (5) What are the values of these functions as $T \rightarrow 0$ and as $T \rightarrow \infty$?

$$(1) q = 1 + e^{-\epsilon/kT}; Q = q^N = (1 + e^{-\epsilon/kT})^N;$$

$$(2) E = N \epsilon e^{-\epsilon/kT} / (1 + e^{-\epsilon/kT});$$

$$(3) S = \frac{N\epsilon e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} \frac{1}{T} + Nk \ln(1 + e^{-\epsilon/kT}) = \frac{N\epsilon}{1 + e^{\epsilon/kT}} \frac{1}{T} + Nk \ln(1 + e^{-\epsilon/kT})$$

$$(4) C_v = \left(\frac{\partial E}{\partial T} \right)_v = \frac{N\epsilon^2}{kT^2} \frac{e^{-\epsilon/kT}}{(1 + e^{-\epsilon/kT})^2}$$

(5) When $T \rightarrow 0$:

$q \rightarrow 1$ (only the ground state is populated); $E \rightarrow 0$; $S \rightarrow 0$ (use l'Hopital's rule, see the example below); and $C_v \rightarrow 0$ (use l'Hopital's rule);

When $T \rightarrow \infty$:

$q \rightarrow 2$; (both states are equally populated); $E \rightarrow N\epsilon/2$; $S \rightarrow Nk \ln 2$; and $C_v \rightarrow 0$.

Example:

$$\lim_{T \rightarrow 0} S = N\epsilon \lim_{T \rightarrow 0} \frac{1}{(1 + e^{\epsilon/kT})T} + 0 = N\epsilon \lim_{T \rightarrow 0} \frac{\frac{d}{dT} \left(\frac{1}{T} \right)}{\frac{d}{dT} (1 + e^{\epsilon/kT})} = N\epsilon \lim_{T \rightarrow 0} \frac{\frac{1}{T^2}}{\frac{\epsilon}{T^2} e^{\epsilon/kT}} = N \lim_{T \rightarrow 0} \frac{1}{e^{\epsilon/kT}} = 0$$

(assuming $\epsilon > 0$)

Problem 2. (20 pts)

As you know, there could be different measures of the average end-to-end distance in a polymer chain. The most frequently used one is $\langle L^2 \rangle^{1/2}$ (the so-called rms distance), but there is no reason why one could not use $\langle L \rangle$. Consider a polymer chain of N segments each of length b . Calculate $\langle L \rangle$ for $N=100$ and compare it with the other distances we know, i.e. with the rms distance $\langle L^2 \rangle^{1/2}$, with the most likely end-to-end distance for the chain (let's call it L_{\max}), and with the contour length of the chain, L_{cont} . How does the ratio of $\langle L \rangle$ to L_{\max} depend on N ?

$\langle L \rangle = \int_0^{\infty} L W(N, L) dL = 4\pi \left(\frac{3}{2\pi b^2 N} \right)^{\frac{3}{2}} \int_0^{\infty} e^{-\frac{3L^2}{2b^2 N}} L^3 dL =$ -- this integral can be converted to $4\pi \left(\frac{2Nb^2}{3\pi^3} \right)^{\frac{1}{2}} \frac{1}{2} \int_0^{\infty} z e^{-z} dz = \left(\frac{8Nb^2}{3\pi} \right)^{\frac{1}{2}}$ by introducing a new variable $z = 3L^2/(2Nb^2)$ (or if it is easier for you, first $y^2 = 3L^2/(2Nb^2)$ and then another variable, $z=y^2$). The calculation is very similar to the one we did in the class for the average speed of a gas particle, $\langle v \rangle$, therefore I will not repeat it here. The result is

$$\langle L \rangle = \sqrt{\frac{8Nb^2}{3\pi}} = b\sqrt{\frac{800}{3\pi}} \approx 9.21b$$

The most probable distance is:

$$L_{\max} = \sqrt{\frac{2Nb^2}{3}} = b\sqrt{\frac{200}{3}} \approx 8.16b$$

The RMS end-to-end distance is:

$$L_{\text{rms}} = \langle L^2 \rangle^{\frac{1}{2}} = \sqrt{Nb^2} = 10b$$

The contour length is $L_{\text{cont}} = Nb = 100b$. The length comparison is then:

$$L_{\max} < \langle L \rangle < \langle L^2 \rangle^{\frac{1}{2}} < L_{\text{cont}}$$

Both $\langle L \rangle$ and L_{\max} are proportional to $N^{1/2}$, therefore their ratio is independent of N :

$$\frac{\langle L \rangle}{L_{\max}} = \sqrt{\frac{8Nb^2}{3\pi}} / \sqrt{\frac{2Nb^2}{3}} = \frac{2}{\sqrt{\pi}}$$

Problem 3. (40 pts) (the so-called “helix-coil transition” problem)

The early models of protein folding assumed that each monomer in the chain can be in either “coil” or “helix” state, denoted by the letters “c” or “h”, respectively. For example, a particular conformation (with 2 monomers in a helix state) could be represented as a string of letters: **chccchccc**...

Assume that the Gibbs free energy of a monomer in the coil state $G_c = 0$, so that the free energy in the helix state is $G_h = \Delta H - T\Delta S$, where ΔH and ΔS are the changes in the enthalpy and the entropy of a monomer when it undergoes the transition $c \rightarrow h$. Let the s be the equilibrium constant for the $c \leftrightarrow h$ transition, i.e. $s = \exp(-G_h/RT)$.

Consider the following two models, representing the two extremes,

Noncooperative model: each monomer can be in either c or h state, independent of its neighbors;

Fully cooperative model (the “all-or-none” model): once one monomer is in any of the two states, c or h, all other monomers are in the same state, i.e. only chains **cccccccc** and **hhhhhhhh** are allowed.

(1) For each of the two models of the helix-coil transition, derive expressions for the partition function as a function of s and the length of the chain N .

(2) For each of the two models of the helix-coil transition, calculate the average number of monomers (let's call it $\langle n_h \rangle$) in the helix state.

(3) **(10-point bonus)** Assuming $\Delta H < 0$ and $\Delta S < 0$ (helix formation is favorable enthalpically but unfavorable entropically), for each model describe (qualitatively!) the temperature dependence of $\langle N_h \rangle$. For example, you can plot schematically how $\langle N_h \rangle$ changes with T when T increases from 0 (a very low temperature) to ∞ (a very high temperature).

Here are some brief answers to these questions:

(1)

Noncooperative model: $Q = (1+s)^N$; (each monomer could be in either state).

Fully cooperative model: $Q = 1 + s^N$; (either all monomers in c or all in h could be in either state).

(2)

Noncooperative model: $\langle N_h \rangle = \frac{s}{Q} \frac{dQ}{ds} = s \frac{d}{ds} \ln Q = N \frac{s}{1+s}$ (similar to how we calculated the average number of bound ligands for multiple binding site problem).

Fully cooperative model: $\langle N_h \rangle = N \frac{s^N}{1+s^N}$.

(3) $s = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H - T\Delta S}{RT}\right)$;

At $T \rightarrow 0$, $s \rightarrow e^{-\Delta H/RT} \rightarrow \infty$, hence $\langle N_h \rangle \rightarrow N$; (all in the helix state) for both models.

At some (transition) temperature T_m : $\Delta H = T_m \Delta S$, so $s = 1$ and $\langle N_h \rangle / N = 1/2$, i.e. half of the monomers are in the helical state (midpoint of the transition).

As T continues increasing, ΔG becomes positive, and $\langle N_h \rangle$ and s decrease further, so most of the monomers will now be in the coil state.

For the noncooperative model, the shape of the transition curve ($\langle N_h \rangle / N$ versus T) is independent of N . Because N is a big number, the transition is much sharper for the fully coop model (because of s^N), the sharpness increases with N .

