SOLUTIONS

YOUR NAME HERE

October 4, 2006

Chem 120B Midterm #1

Definitions and Useful Formulas:

Boltzmann distribution:

$$p_j = \frac{e^{-\beta E_j}}{Q}$$

Partition function:

$$Q = \sum_j e^{-\beta E_j}$$

Average energy:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

Heat capacity:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} = \frac{\langle (\delta E)^2 \rangle}{k_B T^2}$$

Noninteracting, indistinguishable molecules:

$$Q = \frac{q^N}{N!}$$

Equipartition principle:

$$\langle E \rangle = \frac{n}{2} k_B T,$$

where n is the number of quadratic contributions to the energy.
Boltzmann's definition of entropy:

$$S = k_B \ln W$$

For an open cylinder with radius r and length L:

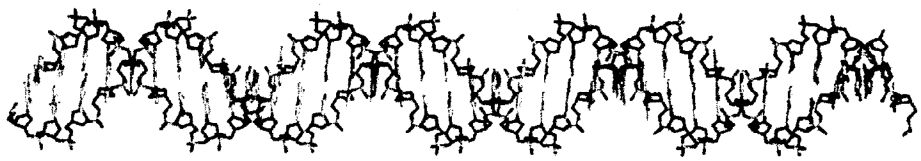
$$\text{volume} = \pi r^2 L, \qquad \text{surface area} = 2\pi r L$$

Some properties of logarithms and exponentials:

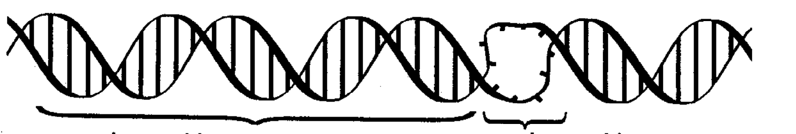
$$\ln x + \ln y = \ln xy, \qquad a \ln x = \ln x^a$$

$$e^a e^b = e^{a+b}, \qquad e^{a \ln x} = x^a$$

This exam consists of **2** questions (both with several parts) on **8** pages. All concern a double-stranded nucleic acid. A small portion of its chemical structure is shown below.



1. The double helix structure is stabilized by binding of bases along one molecule to complementary bases along the other molecule. The picture below highlights this base-pair binding.



In this problem we will assume that each pair of aligned bases is statistically independent. When a pair is unbound, its energy is higher by an amount ϵ, but it can access w_0 times more microscopic states than when it is bound.

10 pts (i) Calculate the partition function for a single pair of bases.

$\underbrace{\text{— — — — —}}_{w_0}$ excited (unbound), $E = \varepsilon$

$E \uparrow$

— ground (bound), $E = 0$

$$Q = e^{-\beta(0)} + w_0 e^{-\beta\varepsilon}$$

$$\Rightarrow \boxed{Q = 1 + w_0 e^{-\beta\varepsilon}}$$

10 pts (ii) Calculate the partition function for a sequence of N bases. Note that different base pairs *can* be distinguished by their position in the sequence.

$$Q = q^N$$

$$\Rightarrow Q = (1 + \omega_o e^{-\beta\varepsilon})^N$$

Difficult (not recommened) alternative:

— $E = N\varepsilon, g = 1$

⋮

— $E = 2\varepsilon, g = \frac{N(N-1)}{2}\omega_o^2$

— $E = \varepsilon, g = N\omega_o$

— $E = 0, g = 1$

$$Q = \sum_{n=0}^{N} \binom{N}{n} \omega_o^n e^{-\beta n\varepsilon}$$

$$= \sum_{n=0}^{N} \binom{N}{n} (\omega_o e^{-\beta\varepsilon})^n$$

$$= (1 + \omega_o e^{-\beta\varepsilon})^N$$

b/c this is simply a binomial series of power N.

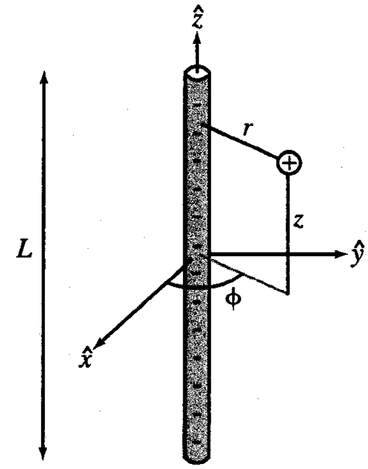
10 pts (iii) From the partition function you calculated in part (ii), calculate the average base-pairing energy for a sequence of N bases as a function of temperature.

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N}$$

$$= -\left[\frac{\partial}{\partial \beta} N \ln(1 + \omega_o e^{-\beta\varepsilon})\right]_{N,V}$$

$$\Rightarrow \boxed{\langle E \rangle = \frac{N\omega_o \varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}}$$

2. Under most conditions phosphate groups along a nucleic acid backbone are negatively charged. In this problem you will consider the double helix to be a rigid rod of length L, with evenly spaced negative charges:



The counterions that balance this negative charge are present in the surrounding solution. Each positive ion is attracted to the nucleic acid through a potential energy

$$u(r) = \sigma \ln\left(\frac{r}{r_0}\right)$$

(which is the sum of attractions to all phosphate groups). As shown above, r is the distance from the ion to the rod; σ and r_0 are positive constants.

10 pts (i) Consider a single ion at a fixed distance r from the rod. With this distance fixed, the ion is confined to the surface of a cylinder with radius r and length L. What is the number of microscopic states, $W(r)$, available for a particle on the surface of this cylinder? (Only the dependence on r is important. You can neglect all other factors.)

$W(r) \propto$ Area of the cylinder

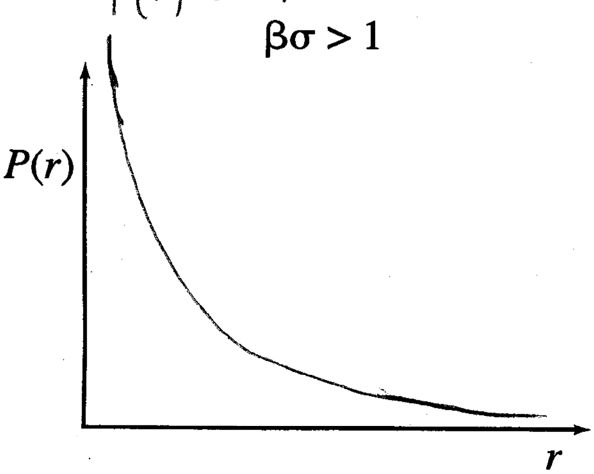
$\Rightarrow$ $\boxed{W(r) = Cr \quad \text{where } C \text{ is independent of } r}$

10 pts (ii) Calculate the probability $P(r)$ of finding an ion at a distance r from the rod. Do not worry about interactions between ions, and do not attempt to normalize the distribution. Write your answer in terms of r, temperature T (or inverse temperature β), and the constants σ and r_0.

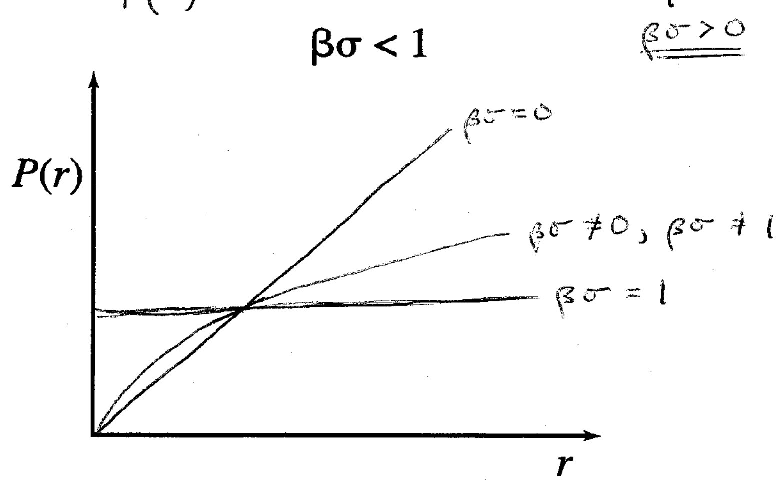
$$P(r) = W(r)e^{-\beta u(r)}$$
$$= C r e^{-\beta\sigma \ln(r/r_0)}$$
$$= C \cdot r \cdot \left(\frac{r}{r_0}\right)^{-\beta\sigma}$$
$$\Rightarrow \boxed{P(r) = (C r_0^{\beta\sigma})\, r^{1-\beta\sigma}}$$

10 pts (iii) Your result from part (ii) should depend sensitively on the quantity σ/k_BT. Sketch the distribution $P(r)$ below for $\sigma/k_BT > 1$ (for example, $\beta\sigma = 3$) and for $\sigma/k_BT < 1$ (for example, $\beta\sigma = 0$).

$P(r) \propto 1/r^x$ where $x > 1$



$P(r) \propto r^x$ where $0 < x < 1$



10 pts (iv) When ions are highly concentrated around the nucleic acid, it is reasonable to replace the potential $u(r)$ with an effective quadratic energy

$$u_{\text{eff}}(r) = \frac{1}{2}kr^2 = \frac{1}{2}k\left(x^2 + y^2\right),$$

where k is another positive constant. Use the equipartition theorem to estimate the heat capacity due to motion of a single ion in this situation. Note that motion in the z-direction is unrestricted. Explain your reasoning. (Hint: When counting an ion's degrees of freedom, use Cartesian coordinates.)

We can write the hamiltonian as,

$$H = KE + PE$$

$$= \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z\right) + \frac{1}{2}k\left(x^2+y^2\right)$$

Since there are 5 squared terms in the hamiltonian, we get $\langle E\rangle = 5\left(\frac{1}{2}k_BT\right)$ according to the equipartition thm.

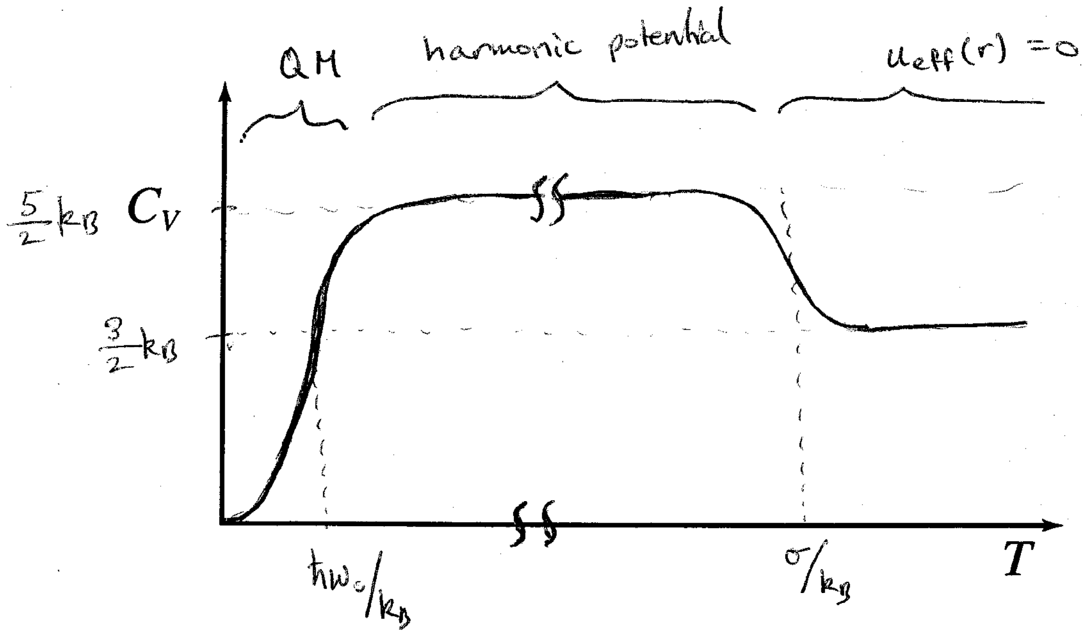
$$\text{So, } C_V = \left(\frac{d\langle E\rangle}{dT}\right)_{N,V} = \frac{d\left(\frac{5}{2}k_BT\right)}{dT} \Rightarrow \boxed{C_V = \frac{5}{2}k_B}$$

10 pts (v) When ions are only weakly attracted to the nucleic acid, the attractive potential $u(r)$ is negligible, so that $u_{\text{eff}}(r) = 0$. According to the equipartition theorem, what is the heat capacity due to motion of a single ion in this situation? Explain your reasoning.

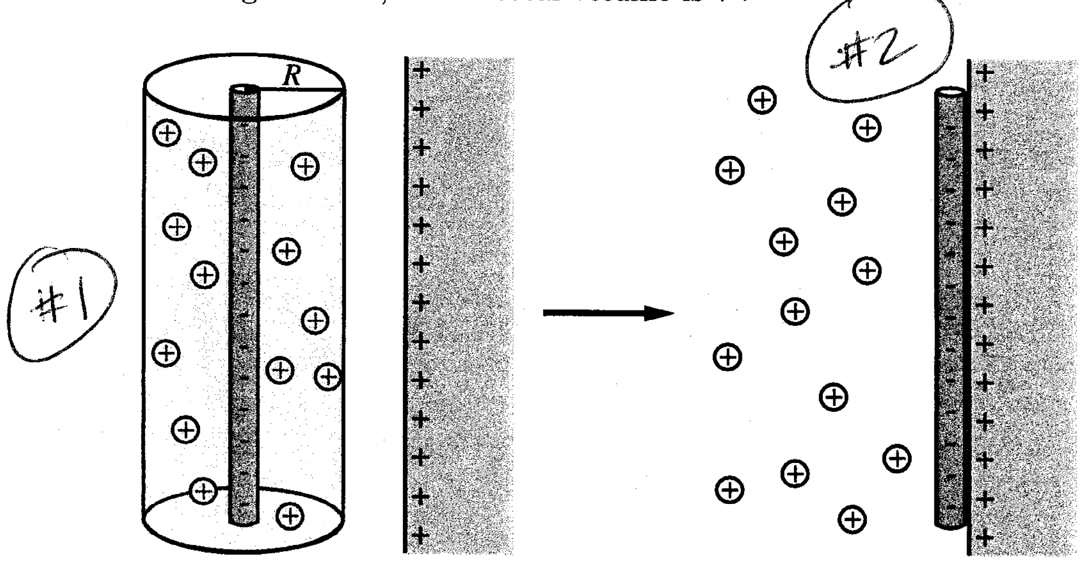
With $u(r) = 0$, $H = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$

Using the same reasoning as above, $\boxed{C_V = \frac{3}{2}k_B}$

10 pts (vi) In the graph below sketch the heat capacity due to motion of a single ion as a function of temperature. Your plot should reflect your results from parts (iv) and (v), as well as your understanding of heat capacity at low temperature. Mark the temperatures $T = 0$ and $T = \sigma/k_B$ on the horizontal axis.



10 pts (vii) Consider N cations whose attraction to a nucleic acid effectively confines them within a cylinder of radius R and length L. If the nucleic acid binds to a positively charged surface (such as a phospholipid membrane), these ions are "released" into the surrounding solution, whose total volume is V:



Calculate the change in entropy when this occurs, using the following approximations: Initially, the system consists of N noninteracting particles in a cylindrical "box", with an effective potential that is zero inside the cylinder and infinite outside the cylinder. Similarly, the final state corresponds to a system of N noninteracting particles in a box with volume V.

$$W_1 \propto \frac{(\pi R^2 L)^N}{N!} \qquad W_2 \propto \frac{V^N}{N!}$$

$$\Delta S = k_B \ln(W_2) - k_B \ln(W_1)$$

$$= k_B \ln\left(\frac{W_2}{W_1}\right)$$

$$= \boxed{N k_B \ln\left(\frac{V}{2\pi R^2 L}\right)}$$