

Release Date: Thursday, November 5  
 Due Date: Friday, November 13, 5 pm CST

Instructions: You may utilize notes, books, and problem set solutions (both your solutions and the posted solutions). You may not, however, discuss the problems with others. You may upload your solutions in any reasonable, readable format. If you have access to a printer, it may be simplest for you to print the exam, complete it on paper, then photograph/scan your answers. Please contact me if you have any questions.

Problem 1:	/	12
Problem 2:	/	8
Problem 3:	/	8
Problem 4:	/	10
Problem 5:	/	32
Problem 6:	/	30
Total:	/	100

Equations you may find useful:

$$1 = \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$\sigma^2 = \int_{-\infty}^{\infty} dx \frac{(x-\mu)^2}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$S = k_B \ln \Omega$$

$$\beta = \frac{1}{k_B T} = \frac{1}{k_B} \left( \frac{\partial S}{\partial E} \right)_{N,V}$$

$$Q(\beta) = \sum_{\nu} e^{-\beta E(\nu)} \quad [\text{Canonical}]$$

$${}^M C_N = \frac{M!}{N!(M-N)!}$$

$$\mu = \int_{-\infty}^{\infty} dx \frac{x}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q(\beta)} \quad [\text{Canonical}]$$

$$-\beta A = \ln Q \quad [\text{Canonical}]$$

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

$$\ln n! \approx n \ln n - n$$

1. **System size scaling. [12 pts.]** For each of the following, identify the dependence on  $N$ . Answers should be in the form of a proportionality. For example, you might answer that the object is proportional to  $N$ , proportional to  $\ln N$ , proportional to 1, or proportional to some other function of  $N$ . (Saying something is proportional to 1 is another way of saying there is no  $N$  dependence.) For full credit, also provide a brief rationale for each answer.

(i) The number of classical microstates for  $N$  particles to be arranged in a box of size  $V$  with energy  $E$ :  $\Omega(N, V, E)$ . **[2 pts.]**

[Hint: You may want to subdivide the system into  $M$  independent cells, each with volume  $v$ , density  $\rho = N/V$ , and energy density  $\epsilon = E/N$ . Let the number of microstates of one such cell be  $\tilde{\omega}$ . Your answer will involve  $\omega = \tilde{\omega}^{1/\rho v}$ .]

(ii) The entropy of a material with  $N$  particles in a volume  $V$  with energy  $E$ :  $S(N, V, E)$ . **[2 pts.]**

(iii) The Gibbs free energy of a material with  $N$  particles kept at pressure  $p$  and temperature  $T$ :  $G(N, p, T)$ . **[2 pts.]**

(iv) The inverse temperature of a  $N$  particle bath of volume  $V$ :  $\beta = \frac{1}{k_B} \left( \frac{\partial S}{\partial E} \right)_{N, V}$ . **[2 pts.]**

(v) The mean squared length between endpoints of a **one**-dimensional lattice polymer:  $\langle R^2 \rangle$ . As you hopefully recall from homework, each bond of the lattice polymer is equally likely in all directions, irrespective of the other bonds. For a one dimensional polymer that means steps left and right, each occur with probability 1/2. **[2 pts.]**

(vi) The mean squared length between endpoints of a **three**-dimensional lattice polymer:  $\langle R^2 \rangle$ . Each bond is still independent of the others and each of the six directions is still equally likely. **[2 pts.]**

2. **Distributions in the thermodynamics limit. [8 pts.]** Imagine a container of  $N_2$  gas at temperature  $T$ . In between collisions, each molecule has some amount of kinetic energy and potential energy (stored in the vibrational, rotational, and electronic degrees of freedom), but after a collision the molecules can exchange energy with each other. Let  $\epsilon_1$  be the energy of a particular  $N_2$  molecule. The total energy in the gas is computed by summing the single-molecule energy over every molecule:  $E = \sum_i \epsilon_i$ . Imagine you make measurements at different times of  $E$  and of the ratio  $E/\langle E \rangle$ . Assuming the gas is a very large (thermodynamic) system, how does the size of fluctuations in your repeated measurements of  $E$  and  $E/\langle E \rangle$  scale with the size of the system? Explain your answers, perhaps with an analogy to coin flips.

3. **Fluctuating energy and particles. [8 pts., 1 pt. each]** Imagine a system surrounded by a rigid, permeable wall. This system can exchange both energy and particles with a much larger reservoir which has an inverse temperature  $\beta$  and a chemical potential  $\mu$ . Fill in the following blanks in the description of this ensemble.

The equilibrium probability for microstate  $\nu$  is

$$P(\nu) = \begin{cases} \frac{\exp(-\beta E(\nu) + \boxed{\phantom{00}})}{\Xi(\boxed{\phantom{00}}, \boxed{\phantom{00}})}, & \text{if } \boxed{\phantom{00}} \\ 0, & \text{otherwise,} \end{cases}$$

where

$$\Xi = \sum_{\nu \text{ with } V(\nu)=V} \exp(\boxed{\phantom{00}}).$$

Various Legendre transforms of the internal energy yield thermodynamic potentials. A list of such transformations includes:  $E$ ,  $A = E - TS$ ,  $G = E - TS + pV$ ,  $H = E + pV$ ,  $\mathcal{F} = E - \mu N$ ,  $\Phi = E - TS - \mu N$ ,  $W = E + pV - \mu N$ . The partition function  $\Xi$  can be connected to one of these thermodynamic potentials as

$$-k_B T \ln \Xi = \boxed{\phantom{00}}.$$

Let us call that thermodynamic potential  $\ominus$  (so as not to give away the previous answer). A small change in  $\ominus$  could be related to small changes in the three natural variables as

$$d\ominus = \boxed{\phantom{00} d\phantom{00} \phantom{00} d\phantom{00} \phantom{00} d\phantom{00}}.$$

The partition function can furthermore be used as a generating function. The first two derivatives yield

$$\left( \frac{\partial \ln \Xi}{\partial(\beta\mu)} \right)_{T,V} = \boxed{\phantom{00}}$$

and

$$\left( \frac{\partial^2 \ln \Xi}{\partial(\beta\mu)^2} \right)_{T,V} = \boxed{\phantom{00}}.$$

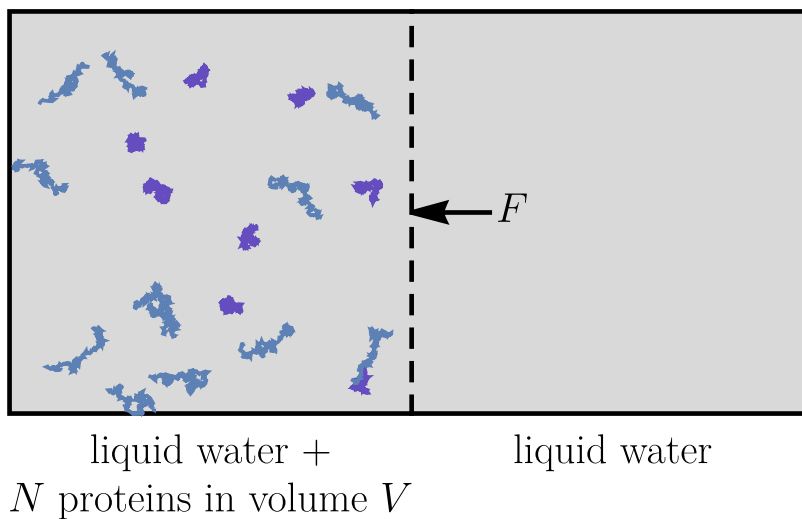
4. **To minimize or not to minimize. [10 pts.]** We are very accustomed to energy minimization as an organizing principle. For example, if you roll a marble down a curved well, it eventually settles into the bottom with zero velocity. A more chemical example is that we expect systems to settle into their lowest-energy electronic ground state. Yet in this course we have come across situations where energy minimization would be misleading.

First, in the case of Hamiltonian dynamics, energy is conserved, and since energy cannot change it is not true that the system relaxes into a minimum energy state. By allowing a system to exchange energy with a bath, we relaxed the constant energy constraint.

- Discuss the applicability of energy minimization as an organizing principle for such a system with fixed  $N$ ,  $V$ , and  $T$ .
- In particular, do you expect the system to minimize its energy  $E$  or would some alternative minimization principle be more applicable? If not  $E$ , what quantity would be minimized?

A good response may include discussion of some or all of the following: entropy, temperature, the Boltzmann distribution, free energy, expectation values, distributions. I am seeking a clear, factual discussion to this slightly open-ended prompt. Incorporate equations or plots if that makes your argument clearer. I expect two or maybe three short paragraphs will suffice.

5. **Proteins in Solution. [30 pts.]** This problem concerns the system drawn schematically below. It is a dilute solution of proteins in water coexisting with pure liquid water at temperature  $T$ . A rigid membrane blocks protein transport while allowing water to pass. The volume of the protein solution,  $V$ , can be adjusted by modifying the force  $F$  applied to the membrane, but the number of protein molecules in the solution,  $N$  cannot change. The presence of proteins in solution causes the pressure pushing on the membrane to be larger than the pure liquid pressure by an amount  $\Delta p$ , the so-called osmotic pressure. At equilibrium, the external force must balance the force from this osmotic pressure,  $F = \Delta p \times (\text{area of membrane})$ .



The proteins in this solution are sufficiently dilute to neglect inter-protein correlations. Each protein can exist in either a folded (purple) or unfolded (blue) state, and the populations of the two species fluctuate as folded proteins can transform to unfolded proteins and vice versa. Thus, while the statistics of  $N$  is trivial (it is constant), the statistics for number of folded and unfolded proteins,  $N_f$  and  $N_u$ , respectively, is nontrivial. At a given instant,

$$N_u = \sum_{i=1}^N n_i,$$

where  $n_i = 0$  or  $1$  when the  $i^{\text{th}}$  protein is folded or unfolded, respectively. The probability that a given protein is unfolded is the average value of  $n_i$ , i.e.,  $\langle n_i \rangle$ . Similarly, the probability a given protein is folded is  $1 - \langle n_i \rangle$ .

In this problem, assume that the Boltzmann-weighted sum over microstates (that is to say the canonical partition function) of one of the folded proteins in solution is  $\omega_f e^{-\beta \epsilon_f}$ , where  $1/\beta = k_B T$ , and both  $\omega_f$  and  $\epsilon_f$  are positive constants. Similarly, assume the partition function for one of the unfolded proteins is  $\omega_u e^{-\beta \epsilon_u}$ , where  $\epsilon_u = \epsilon_f + \Delta \epsilon$  and  $\omega_u = g \omega_f$ . The quantities  $\Delta \epsilon$  and  $g$  are also positive constants, and  $g \gg 1$ .

(i) Determine the probability that a given protein in the solution is unfolded. Express your result in terms of  $T$ ,  $N$ ,  $V$ , and pertinent constants (e.g.  $k_B$ ,  $\epsilon_f$ ,  $\Delta\epsilon$ ,  $\omega_f$ ,  $g$ , etc.). **[5 pts.]**

(ii) Determine the equilibrium average number of proteins that are unfolded,  $\langle N_u \rangle$ . Express your result in terms of  $T$ ,  $N$ ,  $V$ , and pertinent constants. **[5 pts.]**

(iii) At any instant, the number of unfolded proteins in the solution differs from its mean by an amount  $\delta N_u = N_u - \langle N_u \rangle$ . In terms of  $T, N, V$ , and pertinent constants, what is the mean square of this fluctuation,  $\langle (\delta N_u)^2 \rangle$ ? **[6 pts.]**

(iv) Determine the covariance  $\langle (\delta N_u)(\delta N_f) \rangle$  in terms of  $T, N, V$ , and any pertinent constants. **[Warning: It's not zero!] [6 pts.]**



(v) The canonical partition function for the solution relative to that of pure solvent in the volume  $V$  (the solution absent proteins) is

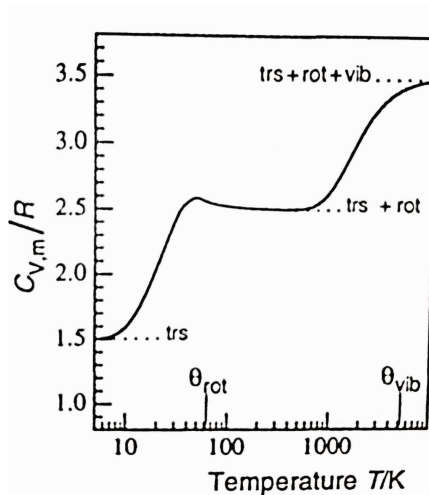
$$Q_{\text{solution}}/Q_{\text{pure water}} = \frac{1}{N!} (V/a^3)^N q^N,$$

where  $a$  is a constant microscopic length (perhaps the largest dimension of a single protein), and

$$q = \omega_{\text{f}} e^{-\beta \epsilon_{\text{f}}} + \omega_{\text{u}} e^{-\beta \epsilon_{\text{u}}}.$$

Starting from the partition function, derive an expression for  $\Delta p$  in terms of  $T$ ,  $N$ ,  $V$ , and pertinent constants. **[10 pts.]**

6. **Heat capacity. [30 pts.]** The heat capacity per mole of a diatomic gas, HD, is plotted below in terms of the gas constant  $R = N_A k_B$ , with  $N_A$  being Avogadro's number.



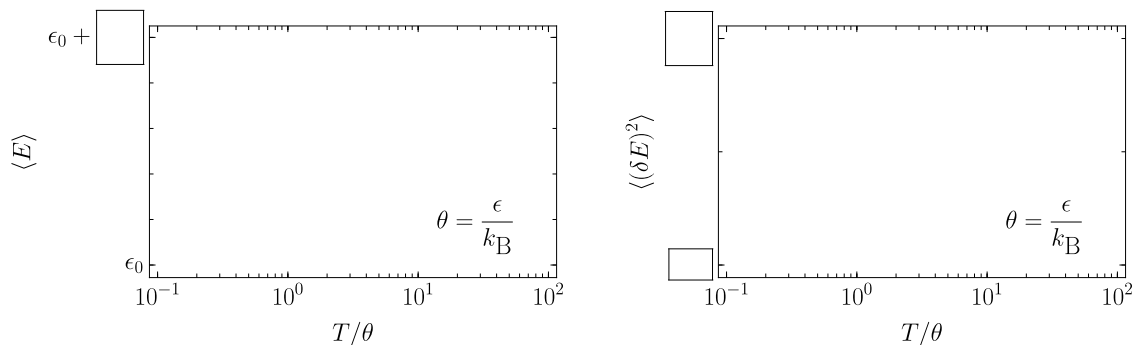
Based on the labels and your chemical intuition, you see that as you move to higher temperatures you “unlock” higher energy states. At low temperatures the molecules have translational motion but are stuck in the ground rotational and vibrational states. At a high enough energy, the rotational excitations start to become relevant, and at a still higher temperature the vibrations also influence the heat capacity.

Todd tries to claim that the HD heat capacity should be simple to understand—the heat capacity should go up the more microstates you unlock. You point out to him that the behavior around  $T = \theta_{rot}$  seems to contradict his simplistic explanation.

The population of the excited states will monotonically increase as temperature increases, but the heat capacity has a peak! This problem will help you convince Todd that a non-monotonic heat capacity is not a concern (and indeed could have been anticipated quite simply).

- (i) The two-state model you studied in Problem Set 6 is a good starting point. Remember, that model has only two possible energy levels that differ in energy by  $\epsilon$ . Demonstrate that the probability of the excited state in the two-state model increases monotonically with temperature. **[5 pts.]**

(ii) *Roughly sketch* plots of average energy  $\langle E \rangle$  and of fluctuations in energy  $\langle \delta E^2 \rangle$  for the two-state model. Fill in the boxes to label the axes with the correct limiting behavior. In case it is not obvious, when I ask for a rough sketch, I'm paying attention to a few distinguishing features like: does it go up, does it go down, what are the low-temperature limits, what are the high-temperature limits, how many peaks does it have, where are the peaks, etc. **[8 pts.]**



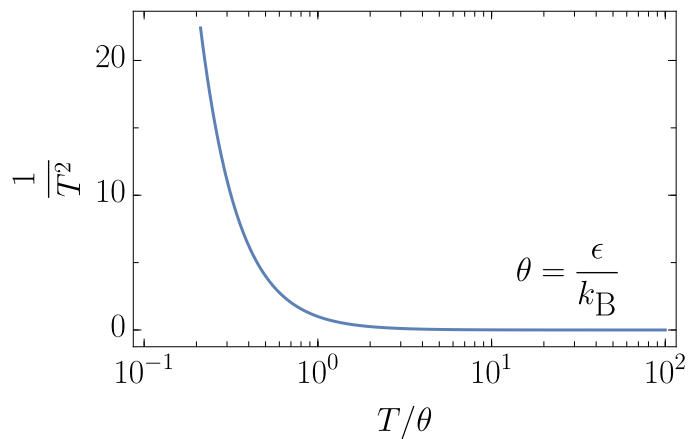
(iii) Derive the two-state model's heat capacity:

$$C_V = \frac{\epsilon^2 e^{-\epsilon/(k_B T)}}{k_B T^2 (1 + e^{-\epsilon/(k_B T)})^2}.$$

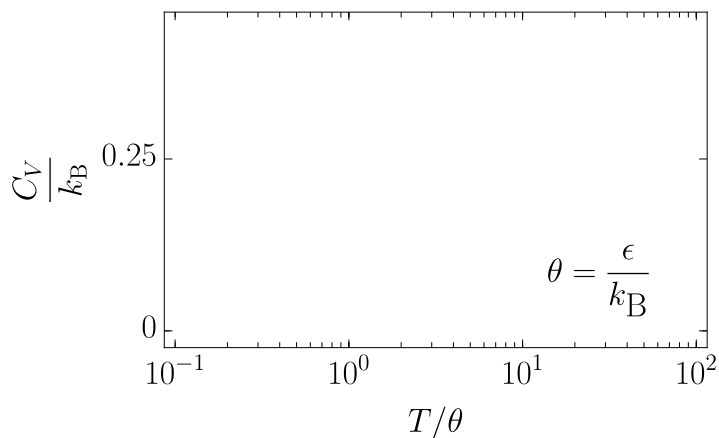
Don't be shy about including some sentences that explain what you are doing in each step. **[5 pts.]**

(iv) Combine results from parts (ii) and (iii) to express  $C_V$  in terms of  $k_B, T$ , and one or more cumulants of energy. [3 pts.]

(v) Use your answers to (ii) and (iv) to *roughly sketch*  $C_V$ . In making your sketch, you will probably find it useful to also think about the plot of  $1/T^2$ :



Do not worry about matching up the height of the  $y$  axis. Take it as given that I have put it on a reasonable scale so that your plot should fill up the space. [4 pts.]



(v) Hopefully by now your work has convinced me that the heat capacity can have non-monotonic features. But your work with the two-state model does not look exactly like the HD heat capacity. One difference is that the HD heat capacity jumps up multiple times; we can easily understand that difference as having to do with new classes of motion (rotations and vibrations) which are unlocked at higher temperatures. The bigger difference is that the high temperature limits do not seem compatible. The HD heat capacity per mole plateaus at  $3.5 k_B$  while your two-state model heat capacity has a different limit. Explain the origin of the difference. **[5 pts.]**