

Date: Thursday, November 10

Instructions: You may utilize notes and problem set solutions (both your solutions and the posted solutions). You may not, however, discuss the problems with others.

Problem 1:	/	12
Problem 2:	/	15
Problem 3:	/	8
Problem 4:	/	30
Problem 5:	/	35
Total:	/	100

Equations you may find useful:

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

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

$$S = k_B \ln \Omega$$

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

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

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

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

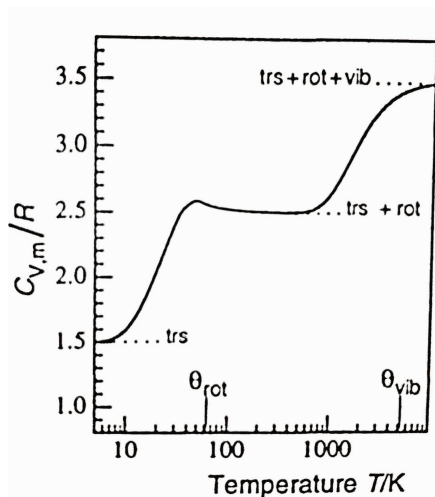
$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q(\beta)} \quad [\text{Canonical}]$$

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

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

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

1. **System size scaling. [12 pts.]**
2. **Protein-ligand binding [15 pts.]**
3. **Fluctuating energy and particles. [8 pts., 1 pt. each]**
4. **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 $T = \theta_{\text{rot}}$ seems to contradict his simplistic explanation.

5. **MOFs. [35 pts.]**

Metal organic frameworks (MOFs) have a wide range of interesting properties stemming from their porous, lattice-like structure. For example, their pores can serve as a host for appropriately sized gas molecules. One thing that MOF chemists love to brag about is their insane surface area, up to 10,000 square meters per gram, meaning about two football fields of area in a paperclip of weight. How can they arrive at such a number? One thing they could do is geometry, approximating pores as cylinders, for example, and using the surface area of those cylinders. You could reasonably wonder if all of that surface area is actually *accessible surface area*, though. To back up claims of accessible surface area, they often perform “isotherm experiments” (at constant temperature) in which they measure the amount of absorbed gas as a function of the applied pressure. From the shape and slopes of that isotherm curve, they infer an effective surface area that the gas could bind and unbind from, as if it were binding to a simple flat 2D surface. In this problem, we build a very simple model of gas absorption to understand how surface area could relate to an isotherm. (The models typically employed for the MOF inference are a little more complicated, but not all that much more so.)