

Problem Set 3

1. Although we will not do so in class, it is possible to derive the partition function for a monatomic van der Waals gas (interacting molecules):

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} (V - Nb)^N e^{aN^2/Vk_B T}$$

where  $a$  and  $b$  are the van der Waals constants. Use this partition function to derive expressions for the average energy,  $\langle E \rangle$ , and heat capacity,  $C_v$ , for the monatomic van der Waals gas.

2. Deriving the partition function for an Einstein crystal is not difficult. Each of the  $N$  atoms of the crystal is assumed to vibrate independently about its lattice position, so that the crystal is pictured as  $N$  independent harmonic oscillators, each vibrating in three directions. The partition function of a harmonic oscillator is

$$\begin{aligned} q_{ho}(T) &= \sum_{v=0}^{\infty} e^{-\beta(v+\frac{1}{2})h\nu} \\ &= e^{-\beta h\nu/2} \sum_{v=0}^{\infty} e^{-\beta h\nu v} \end{aligned}$$

This summation is easy to evaluate if you recognize it as the geometric series:

$$\sum_{v=0}^{\infty} x^v = \frac{1}{1-x}$$

Show that

$$q_{ho}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

and that

$$Q = e^{-\beta U_0} \left( \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right)^{3N}$$

where  $U_0$  is the zero-of-energy where all  $N$  atoms are infinitely separated.

3. Show that the fraction of harmonic oscillators in the ground vibrational state is given by

$$f_0 = 1 - e^{-h\nu/k_B T}$$

and calculate  $f_0$  for  $N_2$  at 300K, 600K, and 1000K. (You'll need to look up the vibrational frequency of  $N_2$  to do this problem.)

4. Plot the fraction of HCl(g) molecules in the first 5 vibrational states at 300 K and 1000 K.

5. The Euler-MacLaurin summation formula is:

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x)dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \dots$$

Let us consider a particle in a 1-d box with  $L = 1$  mm. Define a “translation temperature”

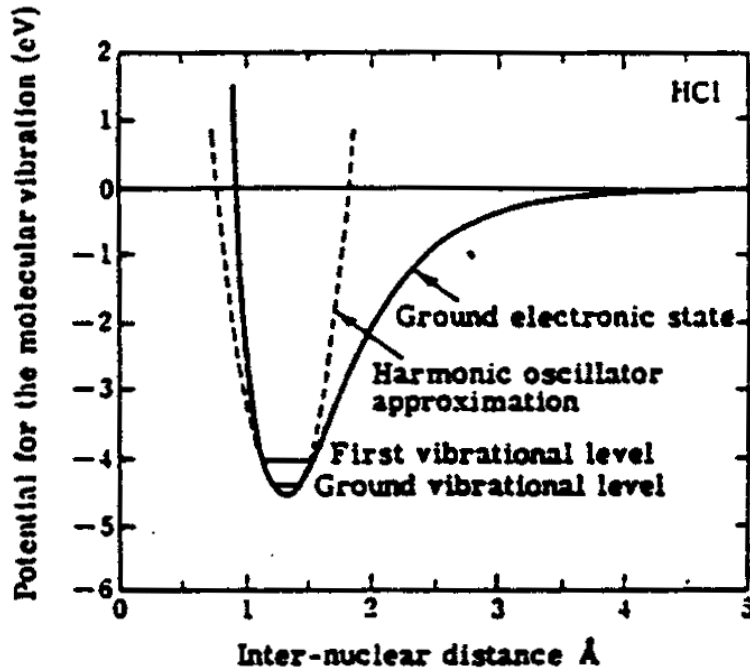
$$T_{tr} = \frac{\hbar^2 2\pi}{ML^2 k_B}$$

Let  $M =$  the mass of a Neon atom. What is  $T_{tr}$ ? At what  $T$  does the integral approximation we made for the translational partition function show any significant error? You can evaluate the low temperature partition function by summing the series.

6. The vibration of a diatomic molecule exhibits anharmonicity when the amplitude becomes very large. This can be seen from the characteristic form of the Morse potential

$$U(r) = D_e \left(1 - e^{-b(r-r_e)}\right)^2$$

where  $D_e$  is the dissociation energy from the bottom of the well,  $r_e$  is the equilibrium bond length.



a) Show that  $b = \nu \sqrt{2\pi^2 \mu / D_e}$  where  $\nu$  is the frequency of the vibration at the equilibrium geometry, and  $\mu$  is the reduced mass of the molecule.

- b) The energy levels of a Morse oscillator can be given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu - x_e \left(n + \frac{1}{2}\right)^2 h\nu \quad (n = 0, 1, 2, \dots)$$

where  $x_e$  is a parameter used to represent the degree of anharmonicity. The dissociation energy from the ground state,  $D_0$  of  $H_2$  is 103.2 kcal / mole, and its fundamental vibrational frequency  $\bar{\omega}$  is 4320  $\text{cm}^{-1}$ . From this information, calculate the values of  $\nu$ ,  $x_e$ , and  $n_{max}$  for  $H_2$ . ( $n_{max}$  is the index of the highest bound state before dissociation).

- c) From the energy expression above, calculate the effect of anharmonicity on the vibrational specific heat up to first order in  $x_e$ .
- d) Extra Credit: Unlike the harmonic oscillator, the Morse oscillator has a finite number of bound states. Write a small computer program to determine numerically the partition function, and average vibrational energy  $H_2$  by summing over all allowed states.