

Ch/ChE 164 Winter 2024 Homework Problem
Set #5 Due Date: Thursday, February 22,
2024 @ 11:59pm PT Out of 100 Points

1. (15 points) (4.15 from Chandler) Consider an isomerization process $A \rightleftharpoons B$, where A and B refer to the different isomer states of a molecule. Imagine that the process takes place in a dilute gas, and that $\Delta\epsilon$ is the energy difference between state A and state B . According to the Boltzmann distribution law, the equilibrium ratio of A and B populations is given by

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{g_A}{g_B} e^{-\beta \Delta\epsilon}, \quad (1)$$

where g_A and g_B are the degeneracies of states A and B , respectively. Show how this same result follows from the condition of chemical equilibria, $\mu_A = \mu_B$.

2. (20 points) (4.16 from Chandler) Consider the system described in problem 1. The canonical partition function is

$$Q = \frac{q^N}{N!} \quad (2)$$

where N is the total number of molecules, and q is the Boltzmann weighted sum over all single molecule states, both those associated with isomers of type A and those associated with isomers of type B .

(a) Show that one may partition the sum and write

$$Q = \sum_P \exp \{ -\beta F(N_A, N_B) \} \quad (3)$$

with

$$-\beta F(N_A, N_B) = \log [(N_A! N_B!)^{-1} q_A^{N_A} q_B^{N_B}], \quad (4)$$

where \sum_P is over all the partitions of N molecules into N_A molecules of type A and N_B molecules of type B , q_A is the Boltzmann weighted sum over states of isomer A , and q_B is similarly defined.

(b) Show that the condition of chemical equilibria is identical to finding the partitioning that minimizes the Helmholtz free energy

$$\frac{\partial F}{\partial \langle N_A \rangle} = \frac{\partial F}{\partial \langle N_B \rangle} = 0 \quad (5)$$

subject to the constraint that $\langle N_A \rangle + \langle N_B \rangle = N$ is fixed.

3. (15 points) (4.25 from Chandler) Use the information compiled in Chapter 8 of Hill's Introduction to Statistical Thermodynamics to calculate the equilibrium constant, K , for the reaction $I_2 \rightleftharpoons 2I$ when the reaction occurs in the dilute gas phase at $T = 1000^\circ\text{K}$. (Note: For the electronic partition function, you need to consider the difference in degeneracies of the ground states of the iodine atom and molecule, $g_{e,I} = 4, g_{e,I_2} = 1$. This is based on the molecular orbital theory. You are not required to show this.)

1

4. (50 pts.) Consider a one-dimensional monatomic crystal of N atoms with equilibrium nearest neighbor spacing a . In order to minimize boundary effects, assume a periodic boundary condition, i.e., $x_{N+1} = x_1$ where x_i is the position of the i th atom. If the atoms interact only with nearest neighbors via a potential $u(x_{i+1} - x_i)$,

(i) show that the energy of the crystal can be written in the form

$$H = \frac{m}{2} \sum_{i=1}^N \dot{\xi}_i^2 + \frac{K}{2} \sum_{i=1}^N (\xi_{i+1} - \xi_i)^2 + Nu(a) \quad (6)$$

to quadratic order in the displacement $\xi_i \equiv x_i - x_i^{(0)}$, where $x_i^{(0)}$ is the equilibrium position of the i th atom. What is K ?

1.1

1.1.1

The third term is fairly simple because it simply describes the interventions of an all of the atoms with their nearest neighbors at alates spacing of a . That is, there are N atoms with a supervision distance from their nearest neighbors of a , so the total energy is $Nu(a)$. The first term represents a kinetic energy of the form $\frac{mv^2}{2}$. But in this case, the velocity we are interested in the first derivative of the displacement distance over a sum over all of the atoms in the cristal.

(ii) Now decompose configurations of atoms into normal modes.

1.1.2

(a) Define normal modes η_k such that ξ_j is a linear superposition of η_k

$$\xi_j = \frac{1}{\sqrt{2N}} \sum_k \eta_k e^{i(jak)} \quad (7)$$

Show that the periodic boundary condition leads to $k = \frac{2\pi n}{Na}$ where n is any integer.

Show further that adding $\frac{2\pi}{a}$ to k does not change ξ_j . Therefore there are only N independent modes. We choose $n \in [-\frac{N}{2}, \frac{N}{2} - 1]$ (assuming N even).

1.2

I think this is similar to how quantization comes from the boundary conditions in the particle in a box.

(b) Show that the fact that the ξ_j 's are real leads to $\eta_k^* = \eta_{-k}$, where η_k^* is the complex conjugate of η_k .

1.3

This has to be related to taking the complex contract of a plain wave exponential.

(iii) It can be shown that the normal mode coordinates η_k diagonalize the Hamiltonian:

$$\sum_j (\xi_{j+1} - \xi_j)^2 = \sum_{k>0} \left[(\eta_k^R)^2 + (\eta_k^I)^2 \right] 4 \sin^2 \left(\frac{1}{2} ka \right) \quad (8)$$

and

$$\sum_j \dot{\xi}_j^2 = \sum_{k>0} \left[(\dot{\eta}_k^R)^2 + (\dot{\eta}_k^I)^2 \right] \quad (9)$$

where η_k^R and η_k^I are the real and imaginary parts of η_k . What is the frequency for each normal mode ω_k ? What is the speed of sound for this model? (The speed of sound is defined as $\left. \frac{d\omega_k}{dk} \right|_{k=0}$).

1.4

The frequencies of the normal moods are going to be given by the agent values of this diagonal matrix.

(iv) Show that in a large 1-D solid, the density (or degeneracy) of normal modes with the frequencies between ω and $\omega + d\omega$ is

$$g(\omega)d\omega = \frac{2N}{\pi\omega_m \sqrt{1 - (\omega/\omega_m)^2}} d\omega \quad (10)$$

where ω_m is the maximum frequency of normal modes.

(v) Compare the Debye model and the exact results.

(a) If one is to make the Debye model for this 1-D solid, what is its Debye temperature Θ_D ? Why is the Debye frequency ω_D larger than the maximum frequency allowed in the system ω_m ?

(b) Show that one gets the same dependency of the heat capacity on temperature at very low temperature with the Debye approximation and with the exact degeneracy. Why does the Debye model give an accurate result even though unphysical normal modes are considered?