Problem Set 5: Chemistry 175/263

This homework is due on Gradescope by class time on Feb. 12, 2025.

1. *Heat Capacity Catastrophe*

Consider a low temperature solid (crystalline or amorphous, like a glass). A defining characteristic of such materials is their relatively small microscopic motions. That is, each atom $\boldsymbol{r}_i$ remains close to its equilibrium position $\boldsymbol{r}_i^{(0)}$. Hence, if we want to describe the position of the atom, it is sensible to write $\boldsymbol{r}_i = \boldsymbol{r}_i^{(0)} + \delta\boldsymbol{r}_i$, where $\delta\boldsymbol{r}_i$ is a small displacement. Within the regime where $\delta\boldsymbol{r}_i$ is small, we can expand an expression for the potential energy of N particles as

$$U(\boldsymbol{r}^N) = U^{(0)} + \frac{1}{2}\sum_{i,j=1}^{N} \delta\boldsymbol{r}_i \cdot K_{ij} \cdot \delta\boldsymbol{r}_j.$$

Note that this is a harmonic (or quadratic) approximation. This formula is hard to use in general because we don't know K_{ij} and its expression could be very complicated. However, if we use a decomposition into "normal modes" in which the Hamiltonian is diagonal, we can simplify the calculation. Let's index the modes by α and denote the αth normal mode by ξ_α. The normal modes are just a new set of coordinates built from linear combinations of the positions. Then the Hamiltonian becomes

$$\mathcal{H} = \sum_{\alpha=1}^{3N} \frac{1}{2} m_\alpha \dot{\xi}_\alpha^2 + \frac{1}{2} m_\alpha \omega_\alpha^2 \xi_\alpha^2$$

where the first term in the summand corresponds to the kinetic energy and the second term in the summand is the potential energy. Here m_α is the "mass" of the normal mode and ω_α is its frequency.

(a) Compute the heat capacity of this system. Note that you can avoid doing any computation if you remember a fact about quadratic degrees of freedom.

(b) You should find that the heat capacity does not depend on temperature. How does this compare with the calculation we did in the free electron model for non-interacting fermions?

(c) The model we are considering is one in which each atom is essentially vibrating around its equilibrium position. At low temperature, approximate the vibrational contribution to the heat capacity assuming that only the vibrational ground state and the first vibrational excited state contribute. Write your expression for a single mode at frequency ω.

(d) To compute the total heat capacity, you need to calculate

$$C_v/k_\mathrm{B} = \frac{1}{k_\mathrm{B}} \int g(\omega) C_v(\omega) d\omega$$

where $g(\omega)$ is the density of states for the system. Assume that only the first normal mode ω_0 contributes to *every* particle. Write an expression for $g(\omega)$. *Hint*: you may want to use the Dirac δ function.

(e) Using your expression for $g(\omega)$ write an expression for the heat capacity of the system. What happens in the limit that $T \longrightarrow 0$. Is this better or worse than the result from (a)?

(f) It turns out that this model of independent low-frequency vibrations is not quite enough to recover the experimental scaling of the heat capacity with temperature at low temperatures. The reason is that it neglects collective fluctuations of the whole solid—these collective modes, called phonons, have much lower energy than the individual particle displacements. Phonons are essentially standing waves of continuous acoustic modes, and thus $g(\omega)$ for phonons is proportional to ω^2, just like in the particle in the box model (where the solutions are also standing waves). Write an expression for C_v/k_{B} using this scaling for $g(\omega)$ and determine the scaling exponent of C_v with respect to T. That is $C_v \propto T^x$; find x. The variable of integration is ω so you do not need an an explicit value for the integral. Take advantage of a u-substitution to extract the overall temperature scaling. Why is this scaling different from what we observed in the free electron model of non-interacting fermions?

2. *Electromagnetic Catastrophe*

Before Quantum Mechanics, it was not clear how electromagnetic radiation could come to thermal equilibrium. You may have encountered this fact in QM as the "ultraviolet catastrophe", which observes that classical equipartition predicts that the energy density of electromagnetic radiation in thermal equilibrium diverges as the frequency increases. The electromagnetic field has normal modes which are standing waves (just like the particle in the box solutions). Each wave travels at the speed of light and thus has frequency $\omega = ck$, where k is the magnitude of the wavevector $\hat{k}$.

(a) Using the fact that photons are bosons, write an expression for the average number of photons per eigenstate with frequency ω. Note that it is reasonable to approximate the photons as non-interacting and that, because photons can be created or destroyed spontaneously, assume that $\mu = 0$.

(b) In class we derived an expression for the density of states $g(k)dk = \frac{Vk^2}{2\pi^2}dk$. Use this to derive an expression for $g(\omega)d\omega$. Don't forget the Jacobian!

(c) Calculate the photon energy per unit volume $u(\omega)d\omega$ using your expression for $g(\omega)$, the energy of a photon with frequency ω, and average population of each mode. This is an exciting result, you should get the formula for Planck's Law we presented without derivation near the begin of Chem 173.

(d) At low frequency, how does your result compare with the expectation from classical equipartition?

(e) A high frequency, how does your result compare with the expectation from classical equipartition.

3. *Ising Universality*

We introduced the Ising Hamiltonian for spins with $\sigma_i \in \{-1, 1\}$ of the form

$$\mathcal{H}_{\mathrm{Ising}}(\sigma_1, \ldots, \sigma_N) = -h\sum_{i=1}^{N}\sigma_i - J\sum_{\langle ij\rangle}\sigma_i\sigma_j.$$

Unlike the non-interacting models we have discussed in the class up to this point, the partition function for the Ising model does not factorize in simple single spin contributions.

This model also serves as the basis for analyzing liquid vapor transitions. Consider, instead of spins, occupancy variables $n_i \in \{0, 1\}$. Suppose that there is an attractive interaction between adjacent occupied cells, i.e., there is a term in the Hamiltonian of the form

$$-\epsilon \sum_{\langle ij \rangle} n_i n_j .$$

(a) Assume that the system can exchange material and energy with the environment. Write an expression for the probability of a given microstate $\{n_1, \ldots, n_N\}$.

(b) Find an explicit mapping between the Ising Hamiltonian and this lattice gas model. That is find expressions for ϵ and the chemical potential μ in terms of h and J.