AEP 4230 / PHYS 4230 Statistical Thermodynamics

Practice for Exam 2

Your name: ______________________________

Question 1: ______________________________ /35

Question 2: ______________________________ /15

Question 3: ______________________________ /30

Question 4: ______________________________ /20

Total: ______________________________ /100

During the second prelim, you will have 90 minutes to complete four problems of a similar format and difficulty to the ones on this practice exam.

Timing: 90 minutes.

I. LANGMUIR ISOTHERMS (35 POINTS)

An ideal gas of particles is in contact with the surface of a catalyst.

(a) [5 points] Show that the chemical potential of the gas particles is related to their temperature and pressure via $\mu = k_B T \left(\ln(P/T^{5/2}) + A_0\right)$ with A_0 some constant.

(b) [8 points] If there are N_a distinct adsorption sites on the surface, and each adsorbed particle gains an energy ϵ upon adsorption, show that the grand partition function Q for the two-dimensional gas with a chemical potential μ satisfies $Q = (1 + e^{\beta(\epsilon+\mu)})^{N_a}$.

(c) [7 points] In equilibrium, the gas and surface particles are at the same temperature and chemical potential. Show that the fraction of occupied sites is then given by $f(T, P) = P/(P + P_0(T))$. Find $P_0(T)$.

(d) [10 points] In the grand canonical ensemble, the particle number N is a random variable. Calculate its characteristic function $\langle e^{-ikN} \rangle$ in terms of $Q(\beta\mu)$ and show that

$$\langle N^m \rangle_c = -(k_B T)^{m-1} \frac{\partial^m \mathcal{G}}{\partial \mu^m}, \tag{1}$$

where $\mathcal{G}$ is the grand potential. Hint: $Q(\beta\mu) = \sum_N e^{\beta\mu N} Z(T, N)$.

(e) [5 points] Using the characteristic function, show that

$$\langle N^2 \rangle_c = k_B T \frac{\partial \langle N \rangle}{\partial \mu}\bigg|_T. \tag{2}$$

II. UNUSUAL WAVE DISPERSION FOR COLLECTIVE EXCITATIONS (15 POINTS)

Consider collective excitations such as phonons in a three-dimensional solid. You have been told that they have the unusual dispersion relation $\omega = Ak^n$ where k is the magnitude of the wavevector. Show that the specific heat scales with temperature as $C \sim T^{3/n}$. You may neglect the cutoff frequency of these excitations such that the upper limit of the frequency integrations you evaluate is infinite.

III. LIGHT-MATTER EQUILIBRIUM (30 POINTS)

Consider a system composed of N two-level systems, all with excitation energy ϵ. If a two-level system is in its ground state, then it can transition to the excited state by absorbing a photon of energy $\epsilon = \hbar\omega$. The total rate of absorption transitions is $\Gamma_{\text{abs}} = n(\omega)AN_g$ where A is a constant, $n(\omega)$ is the number of photons at frequency ω, and N_g is the number of atoms in the ground state.

If the two-level system is in its excited state, it can transition to the ground state by two processes: stimulated emission, and spontaneous emission. In stimulated emission, the total rate of downward transitions is $\Gamma_{\text{stim}} = n(\omega)AN_e$ with N_e the number of atoms in the excited state. In spontaneous emission, the total rate of downward transitions is $\Gamma_{\text{spont}} = BN_e$.

(a) [6 points] Write an equation for dN_e/dt and dN_g/dt, the rate of change of the number of excited and ground state two-level systems.

(b) [5 points] Supposing this collection of two-level systems is in thermal equilibrium, write a relationship between N_e and N_g. Hint: The value is given by what you would expect if there were no photons at all and analyzing the two-level system in the canonical ensemble.

(c) [5 points] In equilibrium, find an expression for n in terms of A and B.

(d) [4 points] Find a relationship between B and A using the fact that the photons are also in thermal equilibrium and thus their occupation is described by a Bose-Einstein distribution.

Instead of two-level systems, let us now consider electrons in a semiconductor. The energies of electrons in a semiconductor can be thought of as taking one of two values, a lower energy state v of energy ϵ_v and a higher energy state c of energy ϵ_c. The rate of absorption of a photon of energy $\hbar\omega = \epsilon_c - \epsilon_v$ is given by $\Gamma_{\text{abs}} = An(\omega)f_v(1 - f_c)$ where A is a constant, n is the number of photons and $f_{c,v}$ are the average numbers of electrons in the higher and lower-energy levels. The values of f_c and f_v are goverened by Fermi-Dirac statistics with a chemical potential μ. The rate of stimulated emission is given by $\Gamma_{\text{stim}} = An(\omega)f_c(1 - f_v)$ and the rate of spontaneous emission by $\Gamma_{\text{spont}} = Bf_c(1 - f_v)$.

(e) [3 points] Write an equation for df_c/dt and df_v/dt. In equilibrium, write expressions for f_c and f_v.

(f) [5 points] Find $n(\omega)$ in equilibrium using the rate equation you derived in the previous part.

(g) [2 points] Write a relationship between A and B.

IV. THERMAL EXPANSION OF SOLIDS (20 POINTS)

Consider a solid composed of N atoms in three dimensions. The potential energy of interaction of the system is given by $\Phi(V)$ when all atoms are in their equilibrium positions. Deviations of the atomic positions from equilibrium can be described in terms of superpositions of phonons (normal modes). There are N_p phonon modes. The phonon frequencies are given by ω_j from $j = 1, ..., N_p$.

You are told that when the volume of the system changes, so do the phonon frequencies. This dependence is quantified by the so-called *Gruneisen parameter* γ_j

defined such that

$$\frac{d\omega_j}{dV} = -\gamma_j \frac{\omega_j}{V}. \tag{3}$$

(a) [2 points] What is the internal energy of the system in the absence of phonons?

(b) [6 points] Show that the total internal energy, including phonons, is given by

$$E = \Phi(V) + U, \tag{4}$$

where U, the energy of the phonons, is given as

$$U = \sum_j \left(\frac{\hbar\omega_j}{2} + \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j} - 1} \right). \tag{5}$$

(c) [6 points] At finite temperature, the free energy is a sum of $\Phi(V)$ and the contribution to the free energy from phonons. Write an expression for the total free energy. (The free energy contribution from (a) is the same as the internal energy since the entropy of the non-phononic degrees of freedom can be neglected.)

(d) [6 points] Show that if we take the Gruneisen parameter to be mode-independent ($\gamma_j = \gamma$ for all j) the pressure of the system is given by:

$$p = -\frac{d\Phi}{dV} + \gamma \frac{U}{V}, \tag{6}$$

where U is the internal energy associated with the phonons.