Qualifying exam - August 2011

Statistical Mechanics

You can use one textbook. Please write legibly and show all steps of your derivations.

Problem 1 [15 points]

Consider a substance for which

$$G = ANT^n p^m, \tag{1}$$

where G is the Gibbs free energy, T temperature, p pressure, N the number of particles and A a positive constant. Find the values of n and m, if any, for which the substance is thermodynamically stable.

Problem 2

The water molecule H_2O has a nonlinear structure with a 104.5° angle between the H-O bonds. The molecule has a known mass m and principal moments of inertia I_1, I_2 and I_3.

1. [5 points] How many vibrational degrees of freedom does the molecule have?

2. [15 points] Considering water vapor as an ideal gas, derive an expression for the chemical potential as a function of temperature T, pressure p and the molecular parameters m, I_i ($i = 1, 2, 3$) and ν_j (vibration frequencies). Assume that $kT \gg \hbar^2/I_i$, where k is the Boltzmann constant.

3. [5 points] What is the high-temperature limit of the constant-volume specific heat of water vapor?

Problem 3

Vibrational properties of a solid containing N_a atoms can be represented by a set of $3N_a$ identical (but distinguishable) harmonic quantum oscillators with the same frequency ω. This model of a solid was proposed by Einstein in 1907. As a generalization of the Einstein model, assume that the vibration frequency depends on volume per atom v: $\omega = \omega(v)$.

1. [5 points] Using this generalized model, show that

$$pV = \gamma E, \tag{2}$$

where p is pressure, V is total volume of the solid, E is its total energy, and

$$\gamma = -\frac{d\ln\omega}{d\ln v} \tag{3}$$

is called the Gruneisen constant.

2. [10 points] Calculate the chemical potential of this solid as a function of v and temperature T.

Now consider a particular case of a solid with $\omega = Av^{-\alpha}$, where A and α are constants.

3. [10 points] Calculate the high-temperature limit ($kT \gg \hbar\omega$) of the isothermal compressibility $\beta_T = -\left(\partial \ln v/\partial p\right)_T$.

4. [10 points] A solid containing N_a atoms is reversibly expanded from a volume V_1 to a volume V_2 at a fixed temperature T. Assuming that the temperature is high, i.e. $kT \gg \hbar\omega$, what is the amount of heat absorbed by the solid in this process?

Problem 4

Consider a free electron gas at $T = 0$ K. Suppose its volume is V and the number of electrons is N.

1. [5 points] Show that the total kinetic energy of the gas is

$$U_0 = \frac{3}{5} N \varepsilon_F, \tag{4}$$

where ε_F is the Fermi energy.

2. [10 points] Derive a relation between the gas pressure p and ε_F.

3. [10 points] Show that the isothermal compressibility of the gas, $\beta_T = -\left(\partial \ln V/\partial p\right)_{T,N}$, equals

$$\beta_T = \frac{3V}{2N\varepsilon_F}. \tag{5}$$