Fall 2008

Statistical Mechanics and Thermodynamics

Answer all problems below.

1. (30) A thermodynamic system of N one-dimensional, noninteracting quantum harmonic oscillators is in equilibrium with a heat reservoir at temperature T. Recall that the energy levels for a quantum oscillator are spaced by integer multiples of $\hbar\omega$ and that the minimum oscillator energy is $\frac{1}{2}\hbar\omega$. Calculate the equilibrium internal energy of the system of N oscillators.

2. (40) Recall that the quantum distribution function for a gas of electrons is

$$f_{FD} = \frac{1}{\exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right) + 1},$$

where ε_F is the Fermi energy (the highest energy level of the occupied states of the gas at zero temperature). Consider a typical monoatomic metal that can be modeled by as a three-dimensional lattice of N independent harmonic oscillators (representing the nuclei and bound electrons) plus a gas of N free, noninteracting electrons at some temperature T.

(a) (10) What is the molar specific heat ($c_{V,latt}$) of the *lattice* at room temperature (~300K, where classical statistical mechanics is applicable)?
Hint: The high temperature limit from problem 1 could be useful here (but remember to replace N in your answer to that problem with $3N$ to go to the equivalent system in 3D), OR you can simply consider classical equipartition of energy. Either way, the result should be fairly simple to arrive at.

(b) (15) Given that ε_F of a typical metal is 7 eV, make *qualitative* sketches of f_{FD} versus electron energy ε for T=0 and T~300K. (Note: eV/K.)

(c) (5) From the shape of the second plot (for finite T), estimate roughly the number of electrons in the free electron gas whose energies are shifted by the change in temperature from 0 to T (answer in terms of N, ε_F and k_BT).

(d) (10) Assuming that only the electrons identified in part (c) will have their energies affected by changes in temperature (around some initial value T), and that these electrons behave as an ideal gas, obtain an expression for the molar specific heat ($c_{V,elec}$) of the free electrons in the metal, and estimate the ratio of lattice and electronic specific heats for a typical metal at 300K.
Hint: Start with the heat capacity for a simple (monoatomic) ideal gas and identify the particle number N in that expression with the number of electrons identified in part (c).

3. (30) Vapor pressure is the pressure exerted by a gas on its condensed (e.g., liquid) state when the gas and liquid phases are in equilibrium in a closed container held at temperature T. Assume the liquid gas coexistence curve in the pressure-temperature plane

is described by the Clausius-Clapeyron equation, $\frac{dP}{dT} = \frac{l}{T\Delta v}$, where l is the molar latent heat of vaporization, and Δv is the volume difference between 1 mole of gas and 1 mole of liquid at the point (P,T) on the coexistence curve.

(a) (20) If the gas is assumed to be ideal, and the molar volume of gas is much larger than that of the liquid ($v_{gas} >> v_{liquid}$), obtain an expression for the vapor pressure as a function of temperature, in terms of l and R (the ideal gas constant).

(b) (5) If the container is opened into standard atmosphere, explain qualitatively why a liquid with a large vapor pressure evaporates more rapidly than one with a lower vapor pressure.