# Fifth Problem Set for Physics 846 (Statistical Physics I) 

Fall quarter 2003
Important dates: Oct 30 10:30am-12:18pm midterm exam,
Nov 11 no class, Nov 27 no class, Dec 11 9:30am-11:18am final exam
Due date: Tuesday, Nov 4

## 13. Regelation

A light rigid metallic bar of rectangular cross section lies on a block of ice, extending slightly over each end. The width of the bar is 2 mm and the length of the bar in contact with ice is 25 cm . Two equal masses, each of mass $M$, are hung from the extending ends of the bar. The entire system is at atmospheric pressure and is maintained at a temperature of $T=-2^{\circ} C$. What is the minimum value of $M$ for which the bar will pass through the block of ice by "regelation"? Use that the latent heat of fusion of water is $80 \mathrm{cal} / \mathrm{g}$, that the density of liquid water is $1 \mathrm{~g} / \mathrm{cm}^{3}$ and that ice cubes float with approximately $4 / 5^{\text {th }}$ of their volume submerged.


## 14. Response functions

A system in its solid phase has a Helmholtz free energy per mole, $f_{s}=B /\left(T v^{3}\right)$, and in its liquid phase it has a Helmholtz free energy per mole, $f_{l}=A /\left(T v^{2}\right)$, where $A$ and $B$ are constants, $v=V / n$ is the volume per mole, and $T$ is the temperature.
a) Compute the molar Gibbs free energy density, $g=G / n$, of the liquid and solid phases in its natural variables.
b) Calculate the coexistence curve $P=P(T)$. (Hint: Write all numerical constants as explicit powers of 2 and 3 - otherwise you will end up with very cumbersome expressions.)
c) Calculate the molar volumes, $v_{s}$ and $v_{l}$, of the liquid and solid phase at the liquid-solid phase transition.
d) Calculate the entropies of the liquid and solid phases at the coexistence line as a function of temperature.
e) Explicitly verify the validity of the Clausius-Clapeyron equation for this system.

## 15. Raoult's law

Consider a solution of some non-volatile substance in equilibrium with the vapor of the solvent. If $x_{\text {solvent }}=n_{\text {solvent }} /\left(n_{\text {solvent }}+n_{\text {solute }}\right)$ is the concentration of the solvent, the chemical potential of the solvent in the presence of the solute is

$$
\mu_{l}\left(P, T, x_{\text {solvent }}\right)=\mu_{l}^{(0)}(P, T)+R T \ln x_{\text {solvent }}
$$

where $\mu_{l}^{(0)}(P, T)$ is the chemical potential of the liquid phase of the pure solvent.
a) Derive a differential equation for the vapor pressure of the solvent as a function of the concentration $x_{\text {solvent }}$ at constant temperature. It should have the form $\left(d P / d x_{\text {solvent }}\right)_{\text {coex }}=$ $f\left(x_{\text {solvent }}, v_{g}, v_{s}, T\right)$ with some function $f$ where $v_{g}$ and $v_{s}$ are the molar volumes of the solvent vapor and the liquid solution respectively.
b) Assume that the vapor can be described by an ideal gas law and that the molar volume of the vapor is much larger than the molar volume of the solution $\left(v_{g} \gg v_{s}\right.$.) Integrate the differential equation that you obtained in a) under this approximation.
c) Relate the difference $\Delta P$ between the vapor pressures of the pure solvent and of the solution at the same temperature to the concentration $x_{\text {solute }}=n_{\text {solute }} /\left(n_{\text {solvent }}+n_{\text {solute }}\right)$ of the solute. This relation is called "Raoult's law". It gives an experimental method to determine the concentration of a solute in a solution by measuring vapor pressures.

