1.

A black box[1] numerical method can give you values for P and N as functions of input variables T, V and μ. It is possible to vary the input variables. How can you find the isothermal compressibility at constant T and N

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

from this numerical method?

2.

Reduce the following derivative

$$\left(\frac{\partial P}{\partial U}\right)_{G,N}$$

to a combination of any of the standard quantities α, κ_T, c_P, and c_v, and T, S, P, V, μ, and N.

3.

Consider a container of volume V with N rod-shaped particles. Each of these rods can change its orientation. For reasons of simplicity limit the possible rod orientations to one of the coordinate axes, x, y or z. Denote the number of rods oriented along the x-direction as N_x, etc. and the total number of rods $N = N_x + N_y + N_z$. The temperature of the container is kept constant equal to T. We have absorbed the Boltzmann constant into T so that it has dimensions energy. The Helmholtz free energy of this system is

$$F = T\left[N_x \ln\left(\alpha l b^2 \frac{N_x}{V}\right) + N_y \ln\left(\alpha b^2 l \frac{N_y}{V}\right) + N_z \ln\left(\alpha b^2 l \frac{N_z}{V}\right) + \gamma l b^2 \frac{N_x N_y + N_y N_z + N_z N_x}{V}\right] \quad (1)$$

where l and b characterize the dimensions of each rod which is taken to be shaped as an elongated rectangular prism so that its volume is lb^2 where $l > b$. α and γ, are dimensionless constants.

a) (Warmup) Define the dimensionless volume variable as $\tilde{V} = V/lb^2$ and write down the expression for the Helmholtz free energy divided by T.

Now start at a very low rod concentration $n = N/V$ and add rods (increase N, keep

[1]black box can only be viewed in terms of its inputs and outputs, without any knowledge of its internal workings.

V constant) at a very slow constant rate, so slow that you may always consider the system to be in equilibrium. T is kept constant. To make the notation simpler you may in the following set the dimensionless constants $\gamma = \alpha = 1$.

b) Compute the equilibrium Helmholtz free energy and use it to describe qualitatively how the pressure changes as n is increased. Determine the phase(s) of the system as n changes. Will there be phase transitions? Coexistence of phases? Is so, give quantitative details of the phases such as the orientation of rods, critical concentrations and pressures. Which, if any, quantities are undergoing discontinuous changes as n is increased continuously?

c) Now consider this system at constant N and T and increase the pressure P by very slowly squeezing harder and harder on the container. Assume again that the system is always in equilibrium. V is no longer constant. Use Gibbs free energy to explain what happens as the pressure is increased. Will there be phase transitions as P changes? Which, if any, quantities undergoes discontinuous changes as P is changed. Assume that the rod concentration at low pressure is low. Explain and give quantitative details where possible.

4.

Consider at system of N independent internal degrees of freedom which each can take one of two energy values, $\pm J$, where J is a positive number with units of energy. Denote the number of internal degrees of freedom with energy $\pm J$ for $N_\pm$. $N_+ + N_- = N$. The total internal energy of this system is

$$E = J\left(N_+ - N_-\right)$$

a) Find an expression for the number of different microstates of this system as a function of N and N_+.

b) Find the entropy as a function of temperature T and N. Make the usual assumptions of large N.

c) Compute the heat capacity (for constant N) for this system. Discuss the behavior of the heat capacity in the limits $T \to 0$ and $T \to \infty$.