

1.

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 .

2.

Assume an extensive system, and reduce the following derivative

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

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, each rod can be oriented along 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

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

where V is the dimensionless ratio of the total volume divided by the volume of a single rod. Note that $V > N$ in order for the rods to fit in the container. α and γ , are dimensionless constants.

a) (Warmup) Find an expression for the entropy of this system.

To make the notation simpler you may in the following set the dimensionless constants $\alpha = \gamma = 1$.

In following subproblems b) and c) the objective is to characterize the behavior of the rod-system under different conditions. You may use analytical or numerical methods, or both. You should answer the following questions for each of the subproblems:

- Determine the phase(s) of the system. Give quantitative details such as the concentration of rods with different orientations.

- Are there phase transitions? If so, find the critical concentrations (or pressures). Which quantities, if any, are undergoing discontinuous changes?
- Are there coexistence of phases? If so, which phases are coexisting.
- As a summary, explain briefly in words what is happening to the system as the conditions are changed.

Warnings: Both these subproblems require a lot of work, and are more similar to mini-research tasks than regular exercises. No oblig will pass that do not contain decent attempts at solving these subproblems.

b) Start at a low rod concentration $n = N/V$ and add rods (increase N , keep 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. Answer the questions above as n changes. Hint: Focus first on the (demanding) task of finding the *equilibrium* Helmholtz free energy.

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. Assume that the rod concentration at low pressure is low. Answer the questions above as P changes.

4.

Consider a 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

$$E = J(N_+ - N_-)$$

- 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 $T \rightarrow 0$ and $T \rightarrow \infty$.