Statistical Mechanics Problems for 2021 Spring Qualifier

Short Problem 1

The Gibbs free energy $G = U - TS + PV$ is the most natural thermodynamic potential for a system held at constant temperature and constant pressure. The thermodynamic relation for G is $dG = -SdT + VdP + \mu dN$.

(a) Derive the thermodynamic relation for dG (above) starting from the thermodynamic relation for U.

(b) The fact that G and N are extensive while T and P are intensive, imply that

$G(T, P, \lambda N) = \lambda G(T, P, N)$. Use this to deduce that $G = N\mu$, where μ is the chemical potential.

Short Problem 2

The Dieterici equation of state for a gas is given below:

$$P = \frac{RT}{(v-b)} e^{\frac{-a}{RTv}}$$

where P is the pressure; R is the universal gas constant; v is the specific volume; T the temperature; and a and b are constants that capture interactions and the finite size of the molecules, respectively.

(a) Show that the critical point can be found at a volume v_C, temperature T_C and pressure P_C given by:

$$v_C = 2b$$

$$T_C = \frac{a}{4Rb}$$

$$P_C = \frac{a}{4e^2 b^2}$$

(b) Describe the physical significance of the critical point.

Long Problem 1

A classical gas at temperature T is in an infinitely high vertical cylinder, which is at rest in a constant gravitational field of acceleration g. If m is the mass of a molecule, then show that the one-molecule partition function is proportional to $(kT)^{5/2}$. Hence, show that the internal energy is that of a classical gas with five degrees of freedom.

Long Problem 2

A system contains 6 particles distributed into three non-degenerate energy levels of $-\varepsilon$, 0, and ε. ($\varepsilon>0$)

For the total energy $E=0$, find the entropy of the system if

(a) the particles are non-distinguishable;
(b) the particles are distinguishable.

Whenever you need it, Gaussian integral: $\int_0^\infty e^{-a^2x^2}\,dx = \frac{\sqrt{\pi}}{2a}$ or $\int_0^\infty x^2 e^{-a^2x^2}\,dx = \frac{\sqrt{\pi}}{4a^3}$