PHYS 301
Thermodynamics and Statistical Mechanics

Problems #15

Wednesday, 05/06/2026

Question 1.

Maxwell's Relations: There are *universal* and non-trivial relationships between different thermodynamics quantities, known as the *Maxwell relations*. We will derive them here, assuming that we keep the particle number N fixed.

(a) First consider the energy function $E = E(S, V)$, which is most naturally written in terms of the entropy S and volume V. The total differential of E is then

$$dE = \left.\frac{\partial E}{\partial S}\right|_V dS + \left.\frac{\partial E}{\partial V}\right|_S dV. \tag{1}$$

From the first law of thermodynamics, we also know that

$$dE = TdS - PdV. \tag{2}$$

We thus have that

$$\left.\frac{\partial E}{\partial S}\right|_V = T, \qquad \left.\frac{\partial E}{\partial V}\right|_S = -P, \tag{3}$$

which are consistent with the relations we have seen long time in statistical mechanics. Use the above to show that

$$\boxed{\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V} \tag{4}$$

(b) Now consider the Helmholtz free energy $F = E - TS$ First, show that

$$dF = -SdT - PdV, \tag{5}$$

and use this to show that

$$\boxed{\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V} \tag{6}$$

(c) How consider the Gibbs free energy $G = F + PV$. First show that

$$dG = -SdT + VdP, \tag{7}$$

and use this to show that

$$\boxed{\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P} \tag{8}$$

(d) Finally consider the enthalpy $H = E + PV$. First show that

$$dH = TdS + VdP, \tag{9}$$

and use this to show that

$$\boxed{\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P} \tag{10}$$