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Physics 151 Problem Set 4

Problem 20

Problem 2.27. More Maxwell relations (Gould and Tobochnik)
From the differentials of the thermodynamic potentials

$$dF = -SdT - PdV,$$

$$dG = -SdT + VdP,$$

$$dH = TdS + VdP,$$

derive the Maxwell relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P,$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.$$

Also consider a variable number of particles to derive the Maxwell relations

$$\left(\frac{\partial V}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N,$$

and

$$\left(\frac{\partial \mu}{\partial V}\right)_N = -\left(\frac{\partial P}{\partial N}\right)_V.$$

Solution:
Given the thermodynamic potential

$$dF = -SdT - PdV \tag{1}$$

We can deduce

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{2}$$

As noted in the textbook, the order of how we take the derivatives does not matter so we have the relation

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \tag{3}$$

Taking the derivatives of the equations in (2) and using the previous relation, we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{4}$$

Similarly, we can repeat the process for the thermodynamic potential dG:

$$dG = -SdT + VdP \tag{5}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \; V = \left(\frac{\partial G}{\partial P}\right)_T \tag{6}$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P} \tag{7}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{8}$$

and dH :

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

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \; V = \left(\frac{\partial H}{\partial P}\right)_S \tag{10}$$

$$\frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P} \tag{11}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P \tag{12}$$

To get the remaining Maxwell relations, we consider the thermodynamic potentials for a gas with N particles. So dG becomes

$$dG = -SdT + VdP + \mu dN \tag{13}$$

At constant T, $dT = 0$ so

$$dG = VdP + \mu dN \tag{14}$$

From this, we get

$$V = \left(\frac{\partial G}{\partial P}\right)_N, \; \mu = \left(\frac{\partial G}{\partial N}\right)_P \tag{15}$$

and a similar relation:

$$\frac{\partial^2 G}{\partial N \partial P} = \frac{\partial^2 G}{\partial P \partial N} \tag{16}$$

Using these equations, we get the following Maxwell relation

$$\left(\frac{\partial V}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N \tag{17}$$

For the last one, we consider the fundamental thermodynamic relation given by

$$dE = TdS - PdV + \mu dN \tag{18}$$

At constant S, $dS = 0$ so

$$dE = -PdV + \mu dN \tag{19}$$

Again doing the same process, we get the relations

$$P = -\left(\frac{\partial E}{\partial V}\right)_N, \ \mu = \left(\frac{\partial E}{\partial N}\right)_V \tag{20}$$

$$\frac{\partial^2 E}{\partial N \partial V} = \frac{\partial^2 E}{\partial V \partial N} \tag{21}$$

which we use to get the final Maxwell relation:

$$\left(\frac{\partial \mu}{\partial V}\right)_N = -\left(\frac{\partial P}{\partial N}\right)_V \tag{22}$$