

Statistical Mechanics

HW 1

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Due: Sept. 9

- (1.1) Derive the Maxwell Relations for the enthalpy H , the Gibbs free energy G , and one of the potentials that also depend on either the particle number or the chemical potential (how many are there?).

For the enthalpy H ,

$$H = U + pV$$

$$\begin{aligned}dH &= dU + pdV + Vdp \\ &= TdS + Vdp\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial H}{\partial S}\right)_p &= T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V \\ \left(\frac{\partial V}{\partial S}\right)_p &= \frac{\partial^2 H}{\partial S \partial p} = \frac{\partial^2 H}{\partial p \partial S} = \left(\frac{\partial T}{\partial p}\right)_S \\ \left(\frac{\partial V}{\partial S}\right)_p &= \left(\frac{\partial T}{\partial p}\right)_S.\end{aligned}$$

For the Gibbs free energy,

$$G = U - TS + pV$$

$$\begin{aligned}dG &= dU - SdT - TdS + pdV + Vdp \\ &= Vdp - SdT\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial G}{\partial p}\right)_T &= V, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S \\ \left(\frac{\partial V}{\partial T}\right)_p &= \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T} = -\left(\frac{\partial S}{\partial p}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial S}{\partial p}\right)_T\end{aligned}$$

We may also derive the Maxwell Relations for the Gibbs free energy that includes

the chemical potential and particle number (the internal energy, enthalpy, Helmholtz free energy, and Grand potential may also include μdN).

$$G = U - TS + pV$$

$$dG = Vdp - SdT + \mu dN$$

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = V, \quad \left(\frac{\partial G}{\partial T}\right)_{p,N} = -S, \quad \left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\frac{\partial^2 G}{\partial p \partial T} = -\frac{\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

$$\left(\frac{\partial S}{\partial N}\right)_{T,p} = -\frac{\partial^2 G}{\partial N \partial T} = -\frac{\partial^2 G}{\partial T \partial N} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,N}$$

$$\left(\frac{\partial V}{\partial N}\right)_{T,p} = \frac{\partial^2 G}{\partial N \partial p} = \frac{\partial^2 G}{\partial p \partial N} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N}$$

Thus our Maxwell Relations are

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N}, \quad \left(\frac{\partial S}{\partial N}\right)_{T,p} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,N}, \quad \left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N}$$

- (1.2) Consider a sample gas in a cylinder of fixed volume and temperate. The cylinder is divided into two chambers with a movable piston in between. Assuming thermodynamic equilibrium at all times and no external forces, which thermodynamic potential is minimized when the piston is standing still?

Let's look at the Helmholtz free energy for this system

$$\begin{aligned} dF &= dU - SdT - Tds \\ &= dQ - pdV - SdT - TdS \end{aligned}$$

At fixed V , and T , the Helmholtz free energy is then

$$dF = dQ - TdS.$$

From the second law we know $dQ \leq TdS$, thus we may conclude that

$$dF \leq 0$$

As such, the Helmholtz free energy may only decrease at fixed V , T . At equilibrium (when the piston stops moving), this energy will be at a minimum.