Maxwell Relations

- Take a function $F(x, y)$

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

Now we have

$$\boxed{\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}}$$

- Let's see what this means:

$$dE = đQ + đW$$

$$dE = T\,dS - p\,dV \quad , \quad \text{or}$$

$$T = \left(\frac{\partial E}{\partial S}\right)_V \qquad -p = \left(\frac{\partial E}{\partial V}\right)_S$$

Of course

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S = \frac{\partial^2 E}{\partial S \partial V}$$

- So we see our first Maxwell relation:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

• Similarly, take for example

$$G = E - TS + pV$$

$$dG = -S\,dT + V\,dp$$

So we find from $\partial^2 G/\partial T \partial p = \partial^2 G/\partial p\,\partial T$ that

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

☆ we will use this below

All of the Maxwell relations are summarized on the next slide

☆ The importance of these seemingly mathematical results is that it relates a number of quantities (such as $\partial S/\partial p$) to measurables

• Recall for $V(T,p)$ we have:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

$$\frac{dV}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p dT + \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T dp$$

$$\equiv \beta_p\, dT - \kappa_T\, dp$$

volume expansion coefficient of material $\propto \partial V/\partial T$

compressibility

κ_T determined by speed of sound

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Energy, $E(S, V)$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Enthalpy, $H(S, p)$

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

Free Energy, $F(T, V)$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Gibbs Free Energy $G(T, P)$

- Thus for example

$$\left(\frac{\partial S}{\partial p}\right)_T = \beta_p V$$

naively hard to measure

how much the material expands under heating. Easy to understand

$$\boxed{\text{Knowing } \beta_p,\ K_T \text{ as well as } C_p \text{ and } C_V \text{ is enough to find everything!}}$$

<u>Examples: Warm ups / Defs</u> ① Pressure ② C_p + C_V

① We have worked with the Volume as fcn of temperature and pressure but one could have used $p(T, V)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

Solving for dp

$$dp = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} dT + \frac{1}{\left(\frac{\partial V}{\partial p}\right)_T} dV$$

$$dp = \frac{\beta_p}{K_T} dT - \frac{1}{K_T} dV$$

- More mathematically we have since $dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV$

$$\left(\frac{\partial p}{\partial T}\right)_V = - \frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\beta_p}{\kappa_T} \qquad \left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{1}{\kappa_T}$$

- This is a relation of a mathematical nature. For any three variables constrained by a function (Blundell Appendix C)

$$f(x, y, z) = 0$$

we can solve for one in terms of the other two leading to e.g.

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}} \quad \text{and} \quad \boxed{\left(\frac{\partial x}{\partial z}\right)_y = -\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x}$$

2 The heat capacities

$$đQ = T\,dS$$

- So at constant volume or pressure:

$$dQ_V = T\,dS_V \quad \text{and} \quad dQ_p = T\,dS_p$$

So dividing by dT we have, since $C = dQ/dT$

$$\boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_V} \quad \text{and} \quad \boxed{C_p = T\left(\frac{\partial S}{\partial T}\right)_p}$$