Maxwell Relations

Follow from 2nd derivatives of the thermodynamic potentials

Energy:

$$E(S,V,N) \Rightarrow \left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S,V,N)$$

$$\text{so} \quad \left(\frac{\partial^2 E}{\partial S \partial V}\right)_N = \left(\frac{\partial T}{\partial V}\right)_{S,N}$$

$$\text{but} \quad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -p(S,V,N)$$

$$\text{so} \quad \left(\frac{\partial^2 E}{\partial V \partial S}\right)_N = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

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

Can do the same for any thermodynamic potential

Helmholtz free energy

$$A(T,V,N) \Rightarrow -\left(\frac{\partial A}{\partial T}\right)_{V,N} = S(T,V,N)$$

$$\text{so} \quad -\left(\frac{\partial^2 A}{\partial T \partial V}\right)_N = \left(\frac{\partial S}{\partial V}\right)_{T,N}$$

$$\text{but:} \quad -\left(\frac{\partial A}{\partial V}\right)_{T,N} = p(T,V,N)$$

$$\text{so} \quad -\left(\frac{\partial^2 A}{\partial V \partial T}\right)_N = \left(\frac{\partial p}{\partial T}\right)_{V,N}$$

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

Or <u>Gibbs free energy</u>

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

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

$$\text{but} \quad \left(\frac{\partial G}{\partial N}\right)_{T,\mu} = \mu(T,p,N)$$

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

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

These equivalences, which follow from the independence of the order of taking 2nd derivatives, are called the <u>Maxwell Relations</u>

See Callen Chpt 7 for a complete list

Response functions

specific heat at const volume $C_V = \left(\frac{dQ}{dT}\right)_{V,N} = T\left(\frac{dS}{dT}\right)_{V,N}$

specific heat at const pressure $C_p = \left(\frac{dQ}{dT}\right)_{p,N} = T\left(\frac{dS}{dT}\right)_{p,N}$

isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$

adiabatic compressibility $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N}$

coefficient of thermal expansion $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$

All the above may be viewed as a second derivative of an appropriate thermodynamic potential

$C_V = T\left(\frac{dS}{dT}\right)_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N}$ since $\left(\frac{\partial A}{\partial T}\right)_{V,N} = -S(T,V,N)$

$C_p = T\left(\frac{dS}{dT}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N}$ since $\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S(T,p,N)$

$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N}$ since $\left(\frac{\partial G}{\partial p}\right)_{T,N} = V(T,p,N)$

$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial p^2}\right)_{S,N}$ since $\left(\frac{\partial H}{\partial p}\right)_{S,N} = V(S,p,N)$

$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial p}\right)_N$ since $\left(\frac{\partial G}{\partial p}\right)_{T,N} = V(T,p,N)$

Since all the various thermodynamic potentials can all be derived from one another, the various second derivates must ~~all~~ be related. If we consider cases where N is held constant (as in all the above response functions) then there ~~one only~~ can be only three independent second derivates, for example

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

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

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

All the other second derivatives of the other potentials must be some combination of these three.

Consider C_V we will show how to write it in terms of the above.

Consider Helmholtz free energy $A(T,V)$
since N is kept constant, we will not write it

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

viewing S as a function of T, and V we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

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

$$\Rightarrow \quad C_p = C_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

Now $\quad \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 A}{\partial T\,\partial V} = \left(\frac{\partial p}{\partial T}\right)_V$

and $\quad \left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T = -1 \quad \leftarrow$ (see general result next page)

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

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

$$= C_V - T\frac{(V\alpha)^2}{-V\kappa_T} = C_V + \frac{TV\alpha^2}{\kappa_T}$$

So $\quad \boxed{C_V = C_p - \frac{TV\alpha^2}{\kappa_T}}$

A general result for partial derivatives

Consider any three variables satisfying a constraint

$f(x, y, z) = 0$ $\Rightarrow$ z for example, is function of x and y
or y is function of x, z etc.

$\Rightarrow$ exists a relation between partial derivates of the variables with respect to each other.

constraint $\Rightarrow$ $df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz = 0$

if hold z const, ie $dz = 0$, then

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial f/\partial y)_{x,z}}{(\partial f/\partial x)_{y,z}}$$

if hold y const, ie $dy = 0$, then

$$\left(\frac{\partial z}{\partial x}\right)_y = -\frac{(\partial f/\partial x)_{y,z}}{(\partial f/\partial z)_{y,x}}$$

if hold x const, ie $dx = 0$, then

$$\left(\frac{\partial y}{\partial z}\right)_x = -\frac{(\partial f/\partial z)_{x,y}}{(\partial f/\partial y)_{x,z}}$$

Multiplying together we get

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

(x, y, z) with constraint among them

Solve for $x(y, z)$ or for $y(x, z)$

then $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$ ①

$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$ ②

Suppose vary dx keeping $dz = 0$

① $\Rightarrow dx = \left(\frac{\partial x}{\partial y}\right)_z dy \rightarrow \frac{dy}{dx} = \frac{1}{(\partial x/\partial y)_z}$

② $\Rightarrow dy = \left(\frac{\partial y}{\partial x}\right)_z dx \Rightarrow \frac{dy}{dx} = \left(\frac{\partial y}{\partial x}\right)_z$

$$\Rightarrow \boxed{\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{(\partial x/\partial y)_z}}$$

Similarly we must be able to write κ_S in terms of c_p, κ_T, α

Consider enthalpy $H(S, p)$

$$\left(\frac{\partial H}{\partial p}\right)_S = V(S, p)$$

regarding V as a function of S and p we have

$$dV = \left(\frac{\partial V}{\partial p}\right)_S dp + \left(\frac{\partial V}{\partial S}\right)_p dS$$

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S - \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T$$

$$\kappa_T = \kappa_S - \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T$$

Now $\left(\frac{\partial S}{\partial p}\right)_T = \frac{-\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial V}{\partial T}\right)_p$

and $\left(\frac{\partial V}{\partial S}\right)_p = \frac{(\partial V/\partial T)_p}{(\partial S/\partial T)_p}$

above follows from: $\frac{\partial G}{\partial p} = V(T, p) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$

$-\frac{\partial G}{\partial T} = S(T, p) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

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

or in general $\left(\frac{\partial z}{\partial y}\right)_x = \frac{(\partial z/\partial u)_x}{(\partial y/\partial u)_x}$

substitute in to get

$$\kappa_T = \kappa_S + \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_p} = \kappa_S + \frac{1}{V}\frac{(V\alpha)^2}{c_p/T}$$

$$\kappa_T = \kappa_S + \frac{TV\alpha^2}{c_p}$$

$$\boxed{\kappa_S = \kappa_T - \frac{TV\alpha^2}{c_p}}$$

See Callen for a systematic way to reduce all such derivatives to combinations of c_p, κ_T, α

The main point is not to remember how to do this, but that it can be done! There are only a finite number of independent 2nd derivatives of the thermodynamic potentials! [if consider only ~~mass~~ N fixed, these are only c_p, κ_T, α]

Another useful relation

$$C_V = T\left(\frac{dS}{dT}\right)_V$$

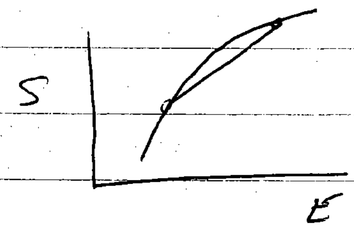
Since $dE = TdS - pdV$ (N fixed) it follows that

$$C_V = \left(\frac{dE}{dT}\right)_V = T\left(\frac{dS}{dT}\right)_V$$

Stability

We already saw that the condition of stability required that $S(E)$ be a concave function

$$\frac{\partial^2 S}{\partial E^2} \leq 0.$$



concave ≡ the cord drawn between any two points on curve lies below the curve

In a similar way, one can show $\frac{\partial^2 S}{\partial V^2} \leq 0$,

or more generally, S is concave in three dimensional S, E, V space

$$S(E+\Delta E, V+\Delta V, N) + S(E-\Delta E, V-\Delta V, N) \leq 2\, S(E, V, N)$$

expanding the ~~right~~ left hand side in a Taylor series we get

$$\frac{\partial^2 S}{\partial E^2}\Delta E^2 + 2\frac{\partial^2 S}{\partial E \partial V}\Delta E \Delta V + \frac{\partial^2 S}{\partial V^2}\Delta V^2 \leq 0$$

For $\Delta V = 0$ this gives $\frac{\partial^2 S}{\partial E^2} < 0$

~~For~~ $\Delta E = 0$ this gives $\frac{\partial^2 S}{\partial V^2} < 0$

More generally, for ΔE and ΔV both $\neq 0$, we can rewrite as

$$(\Delta E, \Delta V)\begin{pmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E \partial V} \\ \frac{\partial^2 S}{\partial E \partial V} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix}\begin{pmatrix} \Delta E \\ \Delta V \end{pmatrix} \leq 0$$

both eigenvalues of the matrix must be ≤ 0

That the quadratic form is always negative implies that and so the determinant of the matrix ~~is negative~~ must be positive ≥ 0

$$\frac{\partial^2 S}{\partial E^2}\frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial E \partial V}\right)^2 \geq 0$$

Note: $\left(\frac{\partial^2 S}{\partial E^2}\right)_V = \frac{\partial}{\partial E}\left(\frac{1}{T}\right)_V = -\frac{1}{T^2}\left(\frac{\partial T}{\partial E}\right)_V = \frac{-1}{T^2 C_V}$

so $\left(\frac{\partial^2 S}{\partial E^2}\right)_V \leq 0 \Rightarrow C_V \geq 0$ specific heat is positive

Other Potentials

One can use the minimization principles of the other thermodynamic potentials, E, A, G, etc to derive other stability criteria.

Energy

S is maximum $\Rightarrow$ E is minimum

S concave $\Rightarrow$ E is convex

$$\Rightarrow \quad E(S+\Delta S, V+\Delta V, N) + E(S-\Delta S, V-\Delta V, N) \geq 2E(S,V,N)$$

$$\Rightarrow \left(\frac{\partial^2 E}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V \geq 0 \quad \text{and} \left(\frac{\partial^2 E}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S \geq 0$$

$$\text{and} \quad \left(\frac{\partial^2 E}{\partial S^2}\right)\left(\frac{\partial^2 E}{\partial V^2}\right) - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 \geq 0$$

$$\text{or} \quad -\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial P}{\partial V}\right)_S - \left(\frac{\partial T}{\partial V}\right)_S^2 \geq 0$$

using $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$, $\left(\frac{\partial p}{\partial V}\right)_S = -\frac{1}{V\kappa_S}$, $\cancel{\left(\frac{\partial T}{\partial V}\right)_S}$

we get

$$\frac{T}{V C_V \kappa_S} \geq \left(\frac{\partial T}{\partial V}\right)_S^2$$

Helmholtz free energy

$$A(T,V,N) = E - TS$$

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = -S \qquad \left(\frac{\partial E}{\partial S}\right)_{V,N} = T$$

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

hence $\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} = -\dfrac{1}{\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N}}$

Since $\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N} \geq 0 \Rightarrow \left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} \leq 0$

E is convex in S $\Rightarrow$ **A is concave in T**

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} = -\left(\frac{\partial S}{\partial T}\right)_{V,N} = -\frac{C_V}{T} \leq 0$$

$$\Rightarrow C_V \geq 0$$

Consider

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

regard p as $p(S(T,V),V)$ from $p = -\dfrac{\partial E(S,V,N)}{\partial V}$

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

Now $\left(\frac{\partial S}{\partial V}\right)_T = -\dfrac{\partial^2 A}{\partial T \partial V} = \left(\frac{\partial p}{\partial T}\right)_V = \dfrac{(\partial p/\partial S)_V}{(\partial T/\partial S)_V}$

So $$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial V}\right)_S + \frac{\left(\frac{\partial p}{\partial S}\right)_V^2}{\left(\frac{\partial T}{\partial S}\right)_V}$$

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

So
$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{\left(\frac{\partial^2 E}{\partial V^2}\right)\left(\frac{\partial^2 E}{\partial S^2}\right) - \left(\frac{\partial E}{\partial V \partial S}\right)^2}{\left(\frac{\partial^2 E}{\partial S^2}\right)_V} \geq 0$$

since E is convex

$$\Rightarrow \left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} \geq 0$$ <u>A is convex in V</u>

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{1}{V\kappa_T} \geq 0 \Rightarrow \kappa_T \geq 0$$

isothermal compressibility must be positive

Gibbs free energy

$$G(T, p, N) = E - TS + pV$$

Legendre transformed from E in both S and V.

$$\Rightarrow \left(\frac{\partial^2 G}{\partial T^2}\right)_p \leq 0 \qquad G \text{ concave in } T$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T \leq 0 \qquad G \text{ concave in } p$$

In general, the thermodynamic ~~potentials~~ free energies (E, A, G, H, Ξ) for constant N (ie E and its legendre transforms) are ~~convex~~ ~~concave~~ convex in their extensive variables (ie S, V) and ~~concave~~ ~~convex~~ concave in their intensive variables (ie T, p).

Le Chatelier's Principle – any ~~\$~~ inhomogeneity that develops in the system should induce a process that tends to eradicate the inhomogeneity. – criterion for stability.