Maxwell Relations

Follow from 2nd derivatives of the thermodynamic potential

Energy:

$E(s, v, n) \Rightarrow \left(\frac{\partial E}{\partial s}\right)_{v, n} = T(s, v, n)$

$\Rightarrow \left(\frac{\partial^2 E}{\partial s \partial v}\right)_{n} = \left(\frac{\partial T}{\partial v}\right)_{s, n}$

but \( \left(\frac{\partial E}{\partial v}\right)_{s, n} = -p(s, v, n) \)

so \( \left(\frac{\partial^2 E}{\partial v \partial s}\right)_{n} = -\left(\frac{\partial p}{\partial s}\right)_{v, n} \)

$\Rightarrow \left(\frac{\partial T}{\partial v}\right)_{s, n} = -\left(\frac{\partial p}{\partial s}\right)_{v, n}$

Can do the same for any thermodynamic potential

Helmholtz free energy

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

$\Rightarrow -\left(\frac{\partial^2 A}{\partial T \partial v}\right)_{n} = \left(\frac{\partial S}{\partial v}\right)_{T, n}$

but, \( \left(\frac{\partial A}{\partial v}\right)_{T, n} = P(T, v, n) \)

$\Rightarrow -\left(\frac{\partial^2 A}{\partial v \partial T}\right)_{n} = \left(\frac{\partial P}{\partial T}\right)_{v, n}$

$\Rightarrow \left(\frac{\partial S}{\partial v}\right)_{T, n} = \left(\frac{\partial P}{\partial T}\right)_{v, n}$
Gibbs free energy

\[ G(T, p, N) \equiv \left( \frac{\partial G}{\partial p} \right)_{T,N} = V(T, p, N) \]

so

\[ \left( \frac{\partial^2 G}{\partial p \partial N} \right)_T = \left( \frac{\partial V}{\partial N} \right)_{T, p} \]

but

\[ \left( \frac{\partial G}{\partial N} \right)_{T, \mu} = \mu(T, p, N) \]

so

\[ \left( \frac{\partial^2 G}{\partial N \partial p} \right)_T = \left( \frac{\partial \mu}{\partial p} \right)_{T,N} \]

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

These equivalences, which follow from the independence of the order of taking 2nd derivatives, are called the Maxwell Relations.

See Callen Chpt 7 for a complete list.
Response functions

Specific heat at constant volume
\[ C_V = \left( \frac{dQ}{dT} \right)_{V,N} = T \left( \frac{dS}{dT} \right)_{V,N} \]

Specific heat at constant pressure
\[ C_P = \left( \frac{dQ}{dT} \right)_{P,N} = T \left( \frac{dS}{dT} \right)_{P,N} \]

Isothermal compressibility
\[ K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

Adiabatic compressibility
\[ K_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S \]

Coefficient of thermal expansion
\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]

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

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

\[ C_P = T \left( \frac{dS}{dT} \right)_P = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{P,N} \quad \text{since} \quad \left( \frac{\partial G}{\partial T} \right)_{P,N} = -S(T,P,N) \]

\[ K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial P^2} \right)_T \quad \text{since} \quad \left( \frac{\partial G}{\partial P} \right)_T = V(T,P,N) \]

\[ K_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S = -\frac{1}{V} \left( \frac{\partial^2 H}{\partial P^2} \right)_S \quad \text{since} \quad \left( \frac{\partial H}{\partial P} \right)_S = V(S,P,N) \]

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left( \frac{\partial^2 G}{\partial T \partial P} \right)_P \quad \text{since} \quad \left( \frac{\partial G}{\partial P} \right)_T = V(T,P,N) \]

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

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

\[
\left( \frac{\partial^2 G}{\partial p^2} \right)_{T, N} = -\nabla V K_T
\]

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

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 \( T \), at \( V \) we have

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

\[\Rightarrow T \left( \frac{\partial S}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_V + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p\]
\[ C_p = C_V + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \]

New:
\[ \frac{\partial S}{\partial V} \bigg|_T = -\frac{\partial^2 A}{\partial T \partial V} = \frac{\partial P}{\partial T} \bigg|_V \]

and
\[ \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial V}{\partial P} \right)_T = -1 \quad \text{(see general result)} \]

So,
\[ \left( \frac{\partial P}{\partial T} \right)_V = -\frac{1}{\left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial V}{\partial P} \right)_T} = -\frac{\left( \frac{\partial V/\partial T}{\partial V/\partial P} \right)_P}{\left( \frac{\partial V/\partial T}{\partial V/\partial P} \right)_T} \]

\[ C_p = C_V + T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V/\partial T}{\partial V/\partial P} \right)_T \]

\[ = C_V - T \left( \frac{V \kappa}{K_T} \right)^2 = C_V + TV \kappa^2 \]

\[ \frac{K_T}{V \kappa} \]

So,
\[ C_V = C_p - TV \kappa^2 \]
A general result for partial derivatives

Consider any three variables satisfying a constraint

\[ f(x, y, z) = 0 \]

\[ \Rightarrow z \text{ for example, is function of } x \text{ and } y \]

or \( y \) is function of \( z \), \( x \), etc.

\[ \Rightarrow \text{ exists a relation between partial derivatives of the variables with respect to each other.} \]

\[
\text{constraint } \Rightarrow \ \frac{df}{dx} = \frac{\partial f}{\partial x} \frac{dx}{dx} + \frac{\partial f}{\partial y} \frac{dy}{dy} + \frac{\partial f}{\partial z} \frac{dz}{dz} = 0
\]

\[ \text{If hold } z \text{ const, i.e. } dz = 0, \text{ then} \]

\[
\left( \frac{\partial x}{\partial y} \right)_z = - \frac{\left( \frac{\partial f}{\partial x} \right)_y}{\left( \frac{\partial f}{\partial y} \right)_x}
\]

\[ \text{If hold } y \text{ const, i.e. } dy = 0, \text{ then} \]

\[
\left( \frac{\partial y}{\partial x} \right)_y = - \frac{\left( \frac{\partial f}{\partial y} \right)_x}{\left( \frac{\partial f}{\partial x} \right)_y}
\]

\[ \text{If hold } x \text{ const, i.e. } dx = 0, \text{ then} \]

\[
\left( \frac{\partial y}{\partial z} \right)_x = - \frac{\left( \frac{\partial f}{\partial y} \right)_z}{\left( \frac{\partial f}{\partial z} \right)_x}
\]

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 \(y(x, z)\)

then \[\begin{align*}
dx &= \left(\frac{\partial x}{\partial y}\right)_z \, dy + \left(\frac{\partial x}{\partial z}\right)_y \, dz \\
dy &= \left(\frac{\partial y}{\partial x}\right)_z \, dx + \left(\frac{\partial y}{\partial z}\right)_x \, dz
\end{align*}\]

Suppose vary \(dx\) keeping \(dz = 0\)

\(\text{1} \Rightarrow d x = \left(\frac{\partial x}{\partial y}\right)_z \, dy \quad \Rightarrow \quad \frac{dy}{dx} = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}\)

\(\text{2} \Rightarrow d y = \left(\frac{\partial y}{\partial x}\right)_z \, dx \quad \Rightarrow \quad \frac{dy}{dx} = \left(\frac{\partial y}{\partial x}\right)_z\)

\[\Rightarrow \left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}\]
Similarly we must be able to write $k_s$ in terms of $g_p, k_T, a$

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

$$dv = \left( \frac{\partial v}{\partial p} \right)_s \, dp + \left( \frac{\partial v}{\partial s} \right)_p \, ds$$

$$-\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_s \left( \frac{\partial s}{\partial p} \right)_T$$

$$k_T = k_s - \frac{1}{v} \left( \frac{\partial v}{\partial s} \right)_p \left( \frac{\partial s}{\partial p} \right)_T$$

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:

$$\frac{\partial g}{\partial p} = v(T, p) \Rightarrow dv = \left( \frac{\partial v}{\partial T} \right)_p \, dT + \left( \frac{\partial v}{\partial p} \right)_T \, dp$$

$$-\frac{\partial g}{\partial T} = s(T, p) \Rightarrow ds = \left( \frac{\partial s}{\partial T} \right)_p \, dT + \left( \frac{\partial s}{\partial p} \right)_T \, dp$$

$$\Rightarrow \left( \frac{\partial v}{\partial s} \right)_p = \frac{(\partial v/\partial T)_p}{(\partial s/\partial T)_p}$$

or in general

$$\left( \frac{\partial y}{\partial x} \right)_x = \frac{(\partial y/\partial u)_x}{(\partial y/\partial u)_x}$$
Substitute \( m \) to get

\[
K_T = K_S + \frac{1}{V} \left( \frac{\partial^2 V}{\partial T} \right)_P \left( \frac{2V}{S} \right)_P = K_S + \frac{1}{V} \left( \frac{V \alpha^2}{C_P/T} \right)_P
\]

\[
K_T = K_S + TV\alpha^2
\]

\[
K_S = K_T - TV\alpha^2
\]

See Callen for a systematic way to reduce all such derivatives to combinations of \( C_P, K_T, \alpha \).

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! [It considers only \( N \) fixed, there are only \( C_P, K_T, \alpha \)].

Another useful relation

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

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

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