cases where \( N \) is held constant (as in all the above response functions) then there can only be only three independent second derivatives, for example

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

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

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

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

\[dS = \left( \frac{\partial S}{\partial T} \right)_{V} + \left( \frac{\partial S}{\partial V} \right)_{T} \, dV\]

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

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

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

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

\[ C_p = C_V \leftrightarrow T \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial V/\partial T}{\partial V/\partial p} \right)_T \]

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

So \[ C_V = C_p - \frac{TV\alpha^2}{K_T} \]
A general result for partial derivatives

Consider any three variables satisfying a constraint

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

\[ \Rightarrow z \text{ for } x, \text{ or } y \text{ is function of } x, z \text{ etc.} \]

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

\[ \text{constraint } \Rightarrow df = \left( \frac{\partial f}{\partial x} \right)_y \delta x + \left( \frac{\partial f}{\partial y} \right)_x \delta y + \left( \frac{\partial f}{\partial z} \right)_x \delta z = 0 \]

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

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

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

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

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

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

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 for \(y(x, z)\)

Then

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

Suppose \(\frac{dx}{dz} = 0\) then \(\frac{dy}{dz} = 0\)

\[
\begin{align*}
\Rightarrow \frac{dx}{dx} &= \left(\frac{\partial x}{\partial y}\right)_z dy \\
\frac{dy}{dy} &= \left(\frac{\partial y}{\partial x}\right)_z dx
\end{align*}
\]

\[
\Rightarrow \left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}
\]
Similarly we must be able to write $K_s$ in terms of $\varphi, K_T, \alpha$

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

$$dV = \left(\frac{\partial V}{\partial p}\right)_s dp + \left(\frac{\partial V}{\partial s}\right)_p ds$$

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

$$K_T = K_s - \frac{1}{V} \left(\frac{\partial V}{\partial s}\right)_p \left(\frac{\partial s}{\partial p}\right)_T$$

Now

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

and

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

above follows from:

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

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

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

or in general:

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

\[ K_T = K_s + \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial V}{\partial T} \right)_p = K_s + \frac{1}{V} \frac{(V \alpha)^2}{C_p/T} \]

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

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

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

\[ C_V = \left( \frac{dE}{dT} \right)_V = T \left( \frac{dS}{dT} \right)_V \]
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 means the chord drawn between any two points on the curve lies below the curve.

In a similar way, one can show \( \frac{\partial^3 S}{\partial V^3} \leq 0 \),
or more generally, $S$ is concave in the three dimensional $S,E,V$ space.

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

Expanding the right hand side in a Taylor series we get

\[ \frac{\partial^3 S}{\partial E^2} \Delta E^2 + 2 \frac{\partial^2 S}{\partial E \partial V} \Delta E \Delta V + \frac{\partial^3 S}{\partial V^3} \Delta V^2 \leq 0 \]

For $\Delta V = 0$ this gives $\frac{\partial^3 S}{\partial E^2} \leq 0$,
For $\Delta E = 0$ this gives $\frac{\partial^3 S}{\partial V^2} \leq 0$.

More generally, for $\Delta E$ and $\Delta V$ both $\neq 0$, we can rewrite as

\[(\Delta E, \Delta V) \left( \begin{array}{cc}
\frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E \partial V} \\
\frac{\partial^2 S}{\partial E \partial V} & \frac{\partial^3 S}{\partial V^2} 
\end{array} \right) (\Delta E, \Delta V) \leq 0 \]
that the quadratic form is always negative implies that the determinant of the matrix must be positive.

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

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

So \[
\left( \frac{\partial^2 S}{\partial E^2} \right)_V \leq 0 \implies C_V > 0 \quad \text{specific heat is positive}
\]

Other Potentials

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

\[ S \text{ max} \implies E \text{ min} \]

\[ S \text{ concave} \implies E \text{ is convex} \]

\[ \implies E(S + \Delta S, V + \Delta V, N) + E(S - \Delta S, V - \Delta V, N) \geq 2E(S, V, N) \]

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

and \[
\left( \frac{\partial^2 E}{\partial S^2} \right)_V \left( \frac{\partial^2 E}{\partial V^2} \right)_S - \left( \frac{\partial^2 E}{\partial S \partial V} \right)^2 \geq 0
\]

\[ -\left( \frac{\partial T}{\partial S} \right)_V \left( \frac{\partial P}{\partial V} \right)_S - \left( \frac{\partial T}{\partial V} \right)^2 \geq 0 \]
Using \( \left( \frac{\partial T}{\partial s} \right)_v = \frac{I}{c_v} \), \( \left( \frac{\partial p}{\partial v} \right)_s = -\frac{1}{V K_s} \), we get

\[
\frac{I}{V c_v K_s} = \left( \frac{\partial T}{\partial v} \right)_s^2
\]
Helmholtz free energy

\[ A(T, V, N) = E - TS \]

\[ \left( \frac{\partial A}{\partial T} \right)_{V,N} = -S \quad \left( \frac{\partial E}{\partial S} \right)_{V,N} = T \]

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

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

since \[ \left( \frac{\partial^2 E}{\partial S^2} \right)_{V,N} > 0 \quad \Rightarrow \quad \left( \frac{\partial^2 A}{\partial T^2} \right)_{V,N} \leq 0 \]

\[ E \text{ is convex in } S \quad \Rightarrow \quad A \text{ is concave in } T \]

Consider \[ \left( \frac{\partial^2 A}{\partial T^2} \right)_{V,N} = -\left( \frac{\partial S}{\partial T} \right)_{V,N} = -\frac{CV}{T} \leq 0 \]

\[ \left( \frac{\partial^2 A}{\partial V^2} \right)_{T,N} = -\left( \frac{\partial P}{\partial V} \right)_{T,N} \quad \Rightarrow \quad CV \geq 0 \]

regard \( p \) as \( p(S(T,V), V) \)

from \[ \frac{\partial p}{\partial V} \]

\[ \Rightarrow \left( \frac{\partial p}{\partial V} \right)_{T} = \left( \frac{\partial p}{\partial V} \right)_{S} + \left( \frac{\partial p}{\partial S} \right)_{V} \left( \frac{\partial S}{\partial V} \right)_{T} \]

Now \[ \left( \frac{\partial S}{\partial V} \right)_{T} = -\frac{\partial^2 A}{\partial T \partial V} = \frac{\partial P}{\partial T} = \frac{(\partial P/\partial S)_{V}}{(\partial T/\partial S)_{V}} \]
\[ S_0 \left( \frac{\partial p}{\partial V} \right)_T = \left( \frac{\partial p}{\partial V} \right)_S + \left( \frac{\partial p}{\partial S} \right)_V \]

\[ \frac{\partial T}{\partial S} \]

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

\[ \left( \frac{\partial^2 E}{\partial S^2} \right)_V \]

\[ S_0 \left( \frac{\partial^2 A}{\partial V^2} \right)_{T,N} = -\left( \frac{\partial p}{\partial V} \right)_{T,N} = \left( \frac{\partial^2 E}{\partial V^2} \right) \left( \frac{\partial^2 E}{\partial S^2} \right) - \left( \frac{\partial E}{\partial V S} \right)^2 \]

\[ \left( \frac{\partial^2 E}{\partial S^2} \right)_V \]

Since \( E \) is convex

\[ \Rightarrow \left( \frac{\partial^2 A}{\partial V^2} \right)_{T,N} \geq 0 \quad \text{A is convex in } V \]

\[ \Rightarrow \left( \frac{\partial^2 A}{\partial V^2} \right)_{T,N} = -\left( \frac{\partial p}{\partial V} \right)_{T,N} = \frac{1}{\sqrt{k_T}} \geq 0 \quad \Rightarrow \quad k_T \geq 0 \]

...thermal compressibility must be positive...
Gibbs free energy

\[ G(T, p, N) = E - TS + PV \]

Legendre transformed from \( E \) in both \( S \) and \( V \).

\[ \frac{\partial^2 G}{\partial T^2} \bigg|_p \leq 0 \quad \text{\( G \) concave in } T \]

\[ \frac{\partial^2 G}{\partial p^2} \bigg|_T \leq 0 \quad \text{\( G \) concave in } p \]

In general, the thermodynamic potentials for constant \( N \) (ie \( E \) and its Legendre transforms) are convex in their extensive variables (ie \( S, V \)) and concave in their intensive variables (ie \( T, p \)).

Le Châtelier's Principle - any inhomogeneity that develops in the system should induce a process that tends to eradicate the inhomogeneity, - criterion for stability.