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**: 
  \[ C_P = \left( \frac{dQ}{dP} \right)_{P,N} = T \left( \frac{dS}{dT} \right)_{P,N} \]

- **Isothermal compressibility**: 
  \[ K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N} \]

- **Adiabatic compressibility**: 
  \[ K_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{S,N} \]

- **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.

- **Specific heat at constant volume**: 
  \[ C_V = T \left( \frac{dS}{dT} \right)_{V,N} = -T \frac{\partial^2 A}{\partial T^2} \] \( V, N \) \[ \text{since} \quad \left( \frac{\partial A}{\partial T} \right)_{V,N} = -S(T, V, N) \]

- **Specific heat at constant pressure**: 
  \[ C_P = \frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_{P,N} = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{P,N} \] \[ \text{since} \quad \left( \frac{\partial G}{\partial T} \right)_{P,N} = -S(T, P, N) \]

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

- **Adiabatic compressibility**: 
  \[ K_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{S,N} = -\frac{1}{V} \left( \frac{\partial^2 H}{\partial T^2} \right)_{S,N} \] \[ \text{since} \quad \left( \frac{\partial H}{\partial P} \right)_{S,N} = V(S, P, N) \]

- **Coefficient of thermal expansion**: 
  \[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N} = \frac{1}{V} \left( \frac{\partial^2 G}{\partial T \partial P} \right)_{P,N} \] \[ \text{since} \quad \left( \frac{\partial G}{\partial P} \right)_{T,N} = V(T, P, N) \]

Since all the various thermodynamic potentials can all be derived from one another, the various second 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:

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

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

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

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

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

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

New:

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

and

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

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

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

\[ = C_V - T (\nu \kappa)^2 = C_V + TV \alpha^2 \]

\[ = C_V - \frac{T (\nu \kappa)^2}{-\nu K \kappa} = C_V + TV \alpha^2 \]

So:

\[ C_V = C_p - \frac{TV \alpha^2}{KT} \]
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 \( x, z \) etc.

\( \Rightarrow \) exists a relation between partial derivatives of the variables with respect to each other.

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

If hold \( z \) const., i.e \( dz = 0 \), then

\[ \left( \frac{\partial^2 x}{\partial y \partial z} \right)_y = - \left( \frac{\partial^2 f}{\partial x \partial y} \right)_{y,z} \]

If hold \( y \) const., i.e \( dy = 0 \), then

\[ \left( \frac{\partial^2 y}{\partial x \partial z} \right)_y = \frac{- \left( \frac{\partial^2 f}{\partial y \partial x} \right)_{y,z}}{\left( \frac{\partial^2 f}{\partial z \partial y} \right)_{x,y}} \]

If hold \( x \) const., i.e \( dx = 0 \), then

\[ \left( \frac{\partial^2 y}{\partial z \partial x} \right)_x = \frac{- \left( \frac{\partial^2 f}{\partial x \partial z} \right)_{x,y}}{\left( \frac{\partial^2 f}{\partial y \partial x} \right)_{y,z}} \]

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 constant among them

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

Then
\[
dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz
\]

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

Suppose \(\text{way } dx\) keeping \(dz = 0\)

\(1 \implies dx = \left(\frac{\partial x}{\partial y}\right)_z dy \implies \frac{dy}{dx} = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}\)

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

\[\implies \left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}\]
Similarly we must be able to write $k_S$ in terms of $g, k_T, \alpha$

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

\[
dV = \left(\frac{\partial V}{\partial P}\right)_S dP + \left(\frac{\partial V}{\partial S}\right)_P dS
\]

\[
-\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T
\]

\[
k_T = k_S - \frac{1}{V} \left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T
\]

Now \(\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial G}{\partial T} = -\left(\frac{\partial V}{\partial T}\right)_P\)

and \(\left(\frac{\partial V}{\partial S}\right)_P = \frac{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_P}\)

above follows from: \(\frac{\partial G}{\partial P} = V(T, P) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \)

\(-\frac{\partial G}{\partial T} = S(T, P) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \)

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

or in general \(\left(\frac{\partial y}{\partial x}\right)_x = \frac{\left(\frac{\partial y}{\partial u}\right)_x}{\left(\frac{\partial y}{\partial u}\right)_x}\)
\[ k_T = k_S + \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V}{\partial T} \right)_P = k_S + \frac{1}{V} \left( \frac{V}{T} \right)_P \]

\[ k_T = k_S + TV \alpha_2 \]

\[ k_S = k_T - TV \alpha_2 \]

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 \( \text{with } N \text{ fixed, there are only } C_P, k_T, \alpha \).]

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 line drawn between any two points on the 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 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

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

For \( \Delta V = 0 \) this gives \( \frac{\partial^2 S}{\partial E^2} \leq 0 \).

For \( \Delta E = 0 \) the gives \( \frac{\partial^2 S}{\partial V^2} \leq 0 \).

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

\[ \mathbf{(\Delta E, \Delta V)} \left( \begin{array}{cc} \frac{\partial^2 S}{\partial E^2} & \frac{\partial S}{\partial E \partial V} \\ \frac{\partial S}{\partial E \partial V} & \frac{\partial^2 S}{\partial V^2} \end{array} \right) \mathbf{(\Delta E, \Delta V)} \leq 0 \]
That the quadratic form is always negative implies that both eigenvalues of the matrix must be \( < 0 \) and so the determinant of the matrix must be positive \( > 0 \)

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

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

So \( \left( \frac{\partial S}{\partial E^2} \right) \geq 0 \Rightarrow C_V > 0 \) 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

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

\( \Rightarrow \left( \frac{\partial^2 E}{\partial S^2} \right) \frac{\partial S}{\partial \nu} \geq 0 \) and \( \left( \frac{\partial^2 E}{\partial E^2} \right) = -\left( \frac{\partial S}{\partial \nu} \right) \geq 0 \)

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

\( \Rightarrow -\left( \frac{\partial S}{\partial \nu} \right) \left( \frac{\partial S}{\partial \nu} \right) \geq 0 \)
Using \( \left( \frac{\partial T}{\partial S} \right)_V = \frac{I}{c_V} \), \( \left( \frac{\partial P}{\partial V} \right)_S = -\frac{1}{\sqrt{\kappa_s}} \), and \( \left( \frac{\partial S}{\partial V} \right)_s \) we get

\[
\frac{I}{\sqrt{c_V \kappa_s}} \gg \left( \frac{\partial T}{\partial V} \right)_s^2
\]
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 \[ \left( \frac{\partial^2 A}{\partial T^2} \right)_{V,N} = -\frac{1}{\left( \frac{\partial E}{\partial S^2} \right)_{V,N}} \]

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

E is convex in S \quad \Rightarrow \quad A is concave in T

Consider

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

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

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

\[ \Rightarrow \left( \frac{\partial P}{\partial V} \right)_T = \left( \frac{\partial P}{\partial V} \right)_S + \left( \frac{\partial P}{\partial S} \right)_N \left( \frac{\partial S}{\partial V} \right)_T \]

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

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

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

\[ S_0 \quad \left( \frac{\partial^2 A}{\partial V^2} \right)_{T,N} = -\left( \frac{\partial p}{\partial V} \right)_{T,N} = \left( \frac{\partial^2 E}{\partial V^2} \left( \frac{\partial^2 E}{\partial s^2} \right) - \left( \frac{\partial E}{\partial v s} \right)^2 \right) \geq 0 \]

\[ \left( \frac{\partial^2 E}{\partial s^2} \right)_V \quad \text{since } E \text{ is convex} \]

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

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

\[ \text{cothermal compressibility must be positive} \]
Gibbs free energy

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

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

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

\[ \left( \frac{\partial^2 G}{\partial P^2} \right)_T \leq 0 \quad G \text{ concave in } P \]

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

Le Chatelier's Principle — any change in homogeneity that develops in the system should induce a process that tends to eradicate the inhomogeneity. — Criterion for stability.