

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

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

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

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

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

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

Since all the various thermodynamic potentials can all be derived from one another, the various second derivatives must ~~all~~ be related. If we consider

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

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

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} = -\kappa/V K_T$$

$$\left(\frac{\partial^2 G}{\partial T \partial P}\right)_N = \gamma \alpha$$

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 , and V we have

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

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

$$\Rightarrow C_p = C_v + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

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

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

$$\text{So } \left(\frac{\partial P}{\partial T} \right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T} = - \frac{\left(\frac{\partial V}{\partial T} \right)_P}{\left(\frac{\partial V}{\partial P} \right)_T}$$

$$C_p = C_v + T \left(\frac{\partial V}{\partial T} \right)_P \frac{\left(\frac{\partial V}{\partial T} \right)_P}{\left(\frac{\partial V}{\partial P} \right)_T}$$

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

So

$$C_v = C_p - \frac{TV\alpha^2}{\kappa_T}$$

A general result for partial derivatives

Consider any three variables satisfying a constraint

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

\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

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

if hold y const, i.e. $dy = 0$, then

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

if hold x const, i.e. $dx = 0$, 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 $y(x, z)$

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

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

Suppose vary x keeping $dz = 0$

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

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

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

Similarly we must be able to write 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

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

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

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

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

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

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

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

$$K_T = K_S + \frac{TV\alpha^2}{C_P}$$

$$K_S = K_T - \frac{TV\alpha^2}{C_P}$$

See Callen for a systematic way to reduce all such derivatives to combinations of C_P , K_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, there are only C_P , K_T , α]

Another useful relation

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

$$\text{Since } dE = TdS - pdV \quad (N \text{ fixed})$$

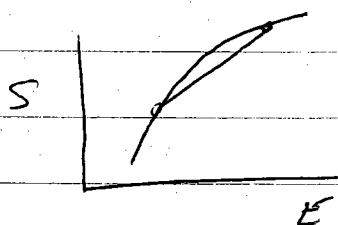
it follows that

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

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 \equiv 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 ~~must be~~ ^{must be} positive ≥ 0

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

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

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

Other Potentials

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

Energy

S is maximum $\Rightarrow E$ is minimum

S concave $\Rightarrow E$ is convex

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

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

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

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

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

we get

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

Helmholtz free energy

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

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

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

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

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

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

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

$$E \text{ is convex in } S \Rightarrow \underline{\underline{A \text{ is concave in } T}}$$

Consider

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

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

$$\Rightarrow C_V \geq 0$$

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

$$\text{from } p = -\frac{\partial E(S, V, N)}{\partial V}$$

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

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

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

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

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

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

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

isothermal compressibility must be positive

Gibbs free energy

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

Legendre transformed from E in both S and V .

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

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

In general, the thermodynamic ^{free energies} potentials for constant N (i.e. E and its Legendre transforms) are ~~convex~~ ^{convex} in their extensive variables (i.e. S, V) and ~~convex~~ ^{concave} in their intensive variables (i.e. T, p). conve;
 concave

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