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

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

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

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

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

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

# A general result for partial derivatives

Consider any three variables satisfying a constraint

$f(x, y, z) = 0$ $\Rightarrow$ $z$ for exagle, is function of $x$ ad $y$
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

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

Similarly we must be able to write $\kappa_S$ in terms of $c_p, \kappa_T, \alpha$

Consider enthalpy $H(S, p)$

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

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 $c_p$, $\kappa_T$, $\alpha$

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! [if consider only ~~mass~~ N fixed, these are only $c_p$, $\kappa_T$, $\alpha$]

Another useful relation

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

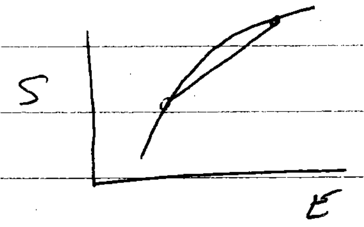
since $dE = TdS - pdV$ (N fixed)
it follows that

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

## Stability

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

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



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

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

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

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

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

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

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

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

both eigenvalues of the matrix must be $\leq 0$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

isothermal compressibility must be positive

## Gibbs free energy

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

Legendre transformed from E in both S and V.

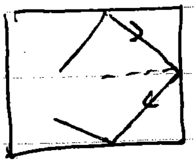
$$\Rightarrow \left(\frac{\partial^2 G}{\partial T^2}\right)_p \leq 0 \qquad G \text{ concave in } T$$

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

In general, the thermodynamic potentials 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 Chatelier's Principle - any inhomogeneity that develops in the system should induce a process that tends to eradicate the inhomogeneity. - criterion for stability.

# Kinetic Theory of ideal gas



pressure $P = \left\langle \frac{\Delta(mv_\perp)}{\text{area}} \cdot \text{rate} \right\rangle$ average over all molecules and time

$\Delta(mv_\perp) = 2mv_\perp$ elastic collision

$\frac{1}{2}\frac{N}{V}v_\perp = \text{rate/area}$

$\uparrow$

$\frac{1}{2}$ towards wall $\qquad \frac{N}{V}$ = uniform density

$$P = 2m\left(\frac{1}{2}\frac{N}{V}\right)\langle v_\perp^2\rangle$$

for isotropic gas $\langle v_\perp^2\rangle = \frac{1}{3}\langle v^2\rangle$

$$P = \frac{1}{3}m\left(\frac{N}{V}\right)\langle v^2\rangle$$

$$= \frac{2}{3}\frac{N}{V}\left\langle \frac{1}{2}mv^2\right\rangle$$

$$= \frac{2}{3}\frac{N}{V}\langle \epsilon_{kinetic}\rangle$$

$$PV = N\frac{2}{3}\langle \epsilon_{kinetic}\rangle$$

$$\Rightarrow \langle \epsilon_{kinetic}\rangle = \frac{3}{2}k_B T$$

## Maxwell velocity distribution (1860)

$p(\vec{v})$ = prob density molec in gas has velocity $\vec{v}$

$$\int d^3v \; p(\vec{v}) = 1$$

a) assume

$$p(\vec{v}) = p_x(v_x)\, p_y(v_y)\, p_z(v_z)$$

$v_x, v_y, v_z$ statistically independent

b) isotropic

assume $p(\vec{v})$ is function only of $v^2$

$$p(\vec{v}) = p_x(v_x)\, p_y(v_y)\, p_z(v_z) = f(v^2) = f(v_x^2 + v_y^2 + v_z^2$$

solution is $p_\mu(v_\mu) \propto C^{v_\mu^2}$ a power

so that $C^{v_x^2} C^{v_y^2} C^{v_z^2} = C^{v^2}$

can always write in the form

$$p_\mu(v_\mu) = C' e^{A v_\mu^2}$$

$A < 0$ prob normalizeabl

$C' > 0$ prob $\geq 0$

$$p(\vec{v}) = C' e^{A v^2}$$

Gaussian distribution define $A = -\frac{1}{2\sigma^2}$ then

$$p_\mu(v_\mu) = \frac{1}{(2\pi)^{1/2}\sigma} e^{-\frac{1}{2}\frac{v_\mu^2}{\sigma^2}}$$

standard deviation $\sigma$

$$\sigma^2 = \langle v_\mu^2 \rangle - \langle v_\mu \rangle^2 \qquad \langle v_\mu \rangle = 0 \text{ by symmetry}$$

$$= \langle v_\mu^2 \rangle = \frac{1}{3} \langle v^2 \rangle = \frac{2}{3m} \langle \tfrac{1}{2} m v^2 \rangle = \frac{2}{3m} \langle \epsilon_{kin}$$

$$= \frac{2}{3m} \frac{3}{2} k_B T = \frac{k_B T}{m}$$

$$p_\mu(v_\mu) = \frac{1}{(2\pi)^{1/2} \sqrt{k_B T/m}} e^{-v_\mu^2/(2 k_B T/m)}$$

$$p(\vec{v}) = p_x(v_x)\, p_y(v_y)\, p_z(v_z)$$

$$p(\vec{v}) = \frac{1}{\left(2\pi \frac{k_B T}{m}\right)^{3/2}} e^{-\frac{m v^2}{2 k_B T}}$$

What is in the exponent is

$\dfrac{\epsilon(\vec{v})}{k_B T}$ where $\epsilon(\vec{v}) = \dfrac{m v^2}{2}$ the kinetic energy of the molecule

(the Boltzmann factor!)