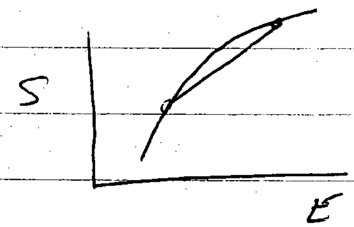
Stability

We already saw that the condition of stability required that $S(E)$ be a <u>concave</u> function

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



concave $\equiv$ the cord drawn between any two points on curve lies <u>below</u> 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 ~~negative~~ positive ≥ 0

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

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

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

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

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

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

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

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

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

isothermal compressibility must be positive

Gibbs free energy

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

Legendre transformed from E in both S and V.

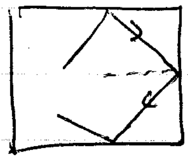
$$\Rightarrow \left(\frac{\partial^2 G}{\partial T^2}\right)_p \leq 0 \qquad G \text{ concave in } T$$

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

In general, the thermodynamic ~~potentials~~ free energies (E, A, G, H, Σ) for constant N (ie E and its legendre transforms) are ~~convex~~ ~~concave~~ convex in their extensive variables (ie S, V) and ~~concave~~ ~~convex~~ 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 = average force per unit area

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

$\Delta(m v_\perp) = 2 m v_\perp$ elastic collision

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

$\frac{1}{2}$ towards wall

$\frac{N}{V}$ = uniform density

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

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

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

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

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

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 ~~of~~ 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 normalizable

$C' > 0$ prob ≥ 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 σ:

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

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

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

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

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

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

what is in the exponent is

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

(the Boltzmann factor!)