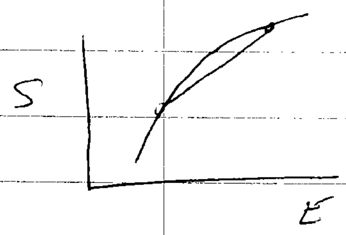
Stability

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 ≡ 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

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

expanding the right 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

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

That the quadratic form is always negative implies that ~~the determinant of the matrix is negative~~ the eigenvalues of the matrix are both negative, so the determinant must be positive

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

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

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

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

and $\left(\frac{\partial^2 E}{\partial S^2}\right)\left(\frac{\partial^2 E}{\partial V^2}\right) - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 \geq 0$ both eigenvalues must be positive

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

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

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

$$\Rightarrow C_V \geq 0$$

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

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

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

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

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

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

isothermal compressibility must be positive

Gibbs free energy

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

Legendre transformed from E in both S and V.

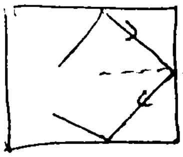
$$\Rightarrow \left(\frac{\partial^2 G}{\partial T^2}\right)_p \leq 0 \qquad G \text{ concave in } T$$

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

In general, the thermodynamic potentials 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 $P = \left\langle \frac{\Delta(m v_\perp)}{\text{area}} \cdot \text{rate} \right\rangle$ 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 $\langle v_\perp^2\rangle = \frac{1}{3}\langle v^2\rangle$

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

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

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

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

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

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 $p(\vec{v})$ a 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 normalizeable

$C' > 0$ 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!)

Statistical Ensembles

How do we make connection between thermodynamics and mechanics?

Ergodic hypothesis

Consider a system of N particles, each with three degrees of freedom, x, y, z. The system is described, in Hamiltonian classical mechanics, by 6N canonical variables

$$q_1, q_2, \ldots, q_{3N}, p_1, \ldots, p_{3N}$$

Hamiltons eqns

$$\left.\begin{aligned} \dot{p}_i &= -\frac{\partial H}{\partial q_i} \\ \dot{q}_i &= \frac{\partial H}{\partial p_i} \end{aligned}\right\} \quad i = 1, \ldots, 3N$$

give the trajectory of the system $\{q_i(t), p_i(t)\}$ in "phase space" – a 6N dimensional space whose coordinates are the q_i and p_i.

In general, total energy will be conserved as the system moves ~~(assuming there are no external time varying~~. The condition $H[q_i, p_i] = E$ defines a 6N-1 dimensional surface in phase space on which the systems trajectory is confined.

If one wanted to compute the ~~average~~ measured value of some quantity, averaged over an interval of time τ, it is:

$$\langle f \rangle = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} dt \; f[q_i(t), p_i(t)]$$

In general, for large N, we expect the trajectory to be some horribly complicated curve on the constant energy surface, that we have no way of computing directly.

To compute $\langle f \rangle$ we therefore need to make an assumption. The ergodic hypothesis says: during any time interval τ, sufficiently long, the location of the system in phase space $\{ q_i(t), p_i(t) \}$ is equally likely to be anywhere on the surface of constant energy E.

Therefore $\langle f \rangle = \int dq_i \, dp_i \; f[q_i, p_i] \; \rho(q_i, p_i)$

where $\rho(q_i, p_i) = C \, \delta\big(H[q_i, p_i] - E \big)$

where C is a normalizing factor such that $\int dq_i \, dp_i \; \rho[q_i, p_i] =$

ρ is called the density matrix.

with the above form, ρ is called the microcanonical ensemble

The ergodic hypothesis cannot in general be proven. But the existence of thermodynamic, as an empirically consistent theory, suggests why it may be true.

By thermodynamics we assume that the macroscopic properties of a system are completely described by a set of a few macroscopic variables, such as total energy E, N, V ~~[illegible]~~ If the ergodic hypothesis were not true, there would be parts of phase space with the same value of E, that never "saw" each other – ie a trajectory in one part would not enter the other, and vice versa. One could imagine, therefore, that systems in these two disjoint regions of phase space might have different properties, ~~[illegible]~~ ie have different time averages of some particular property $f[q,p]$. One therefore might expect them to represent thermodynamically <u>distinguishable</u> states. But this would contradict the assumption that E alone is the important thermodynamic variable.

Alternatively, if ergodicity fails, there might be some other important macroscopic variable (for example magnetization) which one overlooked. The disjoint regions of the constant energy surface could correspond to different values of this new macroscopic variable.

In other words, in the absense of and further information, we assume that all microscopic states $\{q_i, p_i\}$ consistent with a given set of macroscopic thermodynamic variables, E, N, V, are equally likely.

In the ensemble theory one abandons any effort to compute thermodynamic properties from the explicitly time dependent trajectory of the system in phase space. Rather one describes the thermodynamic state as represented by a particular ensemble given by the density matrix $\rho(q_i, p_i)$

The ensemble average $\langle f \rangle = \int dq_i dp_i \, f[q_i, p_i] \, \rho(q_i, p_i)$ is the value one would find not for a single isolated system moving on its trajectory, ~~but for a collection~~ but for the average of a collection of systems distributed in phase space according to the density ρ. The ergodic hypothesis asserts these two types of averages are equal.

$\rho(q_i p_i)$ can be viewed as the probability density that the system will be found in phase space at $\{q_i p_i\}$

Equilibrium is described by a density matrix that does not vary in time.