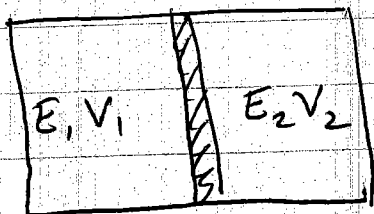


Return to a previous problem

① another way to look at the problem of thermal + mechanical equilibrium



N_1, N_2 fixed so we ignore them

Initially wall is adiabatic and immoveable - subsystems are in equilibrium with energies and volumes E_1, V_1 on left, E_2, V_2 on right

Now wall is allowed to move and to conduct heat.

$$E = E_1 + E_2 \quad \text{stays fixed} \Rightarrow E_2 = E - E_1$$

$$V = V_1 + V_2 \quad \text{stays fixed} \Rightarrow V_2 = V - V_1$$

total entropy is

$$S = S_1(E_1, V_1) + S_2(E - E_1, V - V_1)$$

is maximized when system reaches equilibrium

\Rightarrow equilibrium is when

$$0 = \left(\frac{\partial S}{\partial E_1} \right)_{V_1} = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1} + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2} \frac{\partial E_2}{\partial E_1} = \frac{1}{T_1} - \frac{1}{T_2}$$

$$0 = \left(\frac{\partial S}{\partial V_1} \right)_{E_1} = \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1} + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2} \frac{\partial V_2}{\partial V_1} = \frac{p_1}{T_1} - \frac{p_2}{T_2}$$

$$\Rightarrow T_1 = T_2 \quad \text{and} \quad p_1 = p_2$$

or more specifically, since T and p are functions of E and V ,

$$\begin{cases} T_1(E_1, V_1) = T_2(E-E_1, V-V_1) \\ P_1(E_1, V_1) = P_2(E-E_1, V-V_1) \end{cases}$$

above is two equations for the two unknowns E_1 and V_1 . In principle one can therefore solve them to find E_1 and V_1 (and hence $E_2 = E - E_1$, $V_2 = V - V_1$) of the new equilibrium state.

(2) However, consider the same initial situation, but now the wall is made moveable but stays adiabatic i.e. still no heat can be transported across the wall between the two subsystems. Since $dQ = TdS = 0$ (no heat flows through wall)

$$\Rightarrow dS_1 = dS_2 = 0 \quad \text{total entropy of system cannot change}$$

$$dS_1 = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} dV_1$$

$$= \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 = 0$$

$$\Rightarrow dE_1 = -P_1 dV_1$$

Similarly

$$dE_2 = -P_2 dV_2$$

} energy of each can change only to mechanical done in moving

Total Energy is still conserved $\Rightarrow E = E_1 + E_2$ is fixed
 $\Rightarrow dE_2 = -dE_1$

Total Volume is fixed $\Rightarrow V = V_1 + V_2$ fixed
 $\Rightarrow dV_2 = -dV_1$

$$\left. \begin{aligned} dE_1 &= -p_1 dV_1 \\ dE_2 &= -p_2 dV_2 \Rightarrow -dE_1 = p_2 dV_1 \end{aligned} \right\} \Rightarrow p_1 = p_2$$

$$\text{or } p_1(E_1, V_1) = p_2(E - E_1, V - V_1)$$

in equilibrium the pressures of the two subsystems must be equal - so net force on the wall is zero.

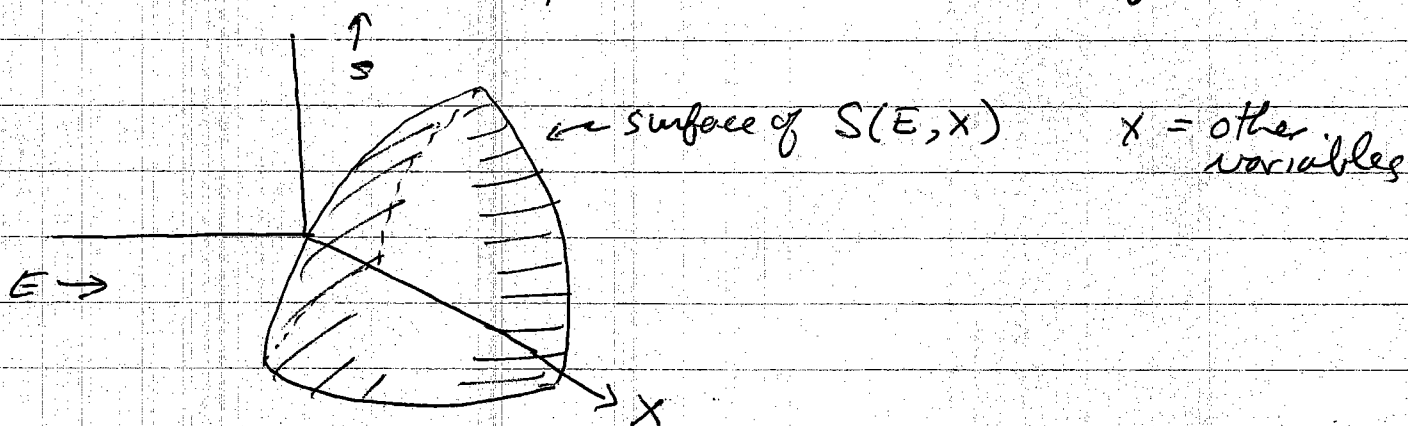
But above is just one equation for two unknown E_1 and V_1 . Thermodynamics alone does not give us enough information to determine the new equilibrium state, [postulate of maximizing the entropy does not help here since total entropy does not change $dS = dS_1 + dS_2 = 0$ when the wall is adiabatic].

The new equilibrium state will depend on details such as the viscosity of the gases in each subsystem. Viscosity is the mechanism by which the energy added to one subsystem via the mechanical work done by the wall goes into increasing the temperature of that gas. If the gases had no viscosity, the wall would just oscillate in simple harmonic motion, and no equilibrium would ever be reached.

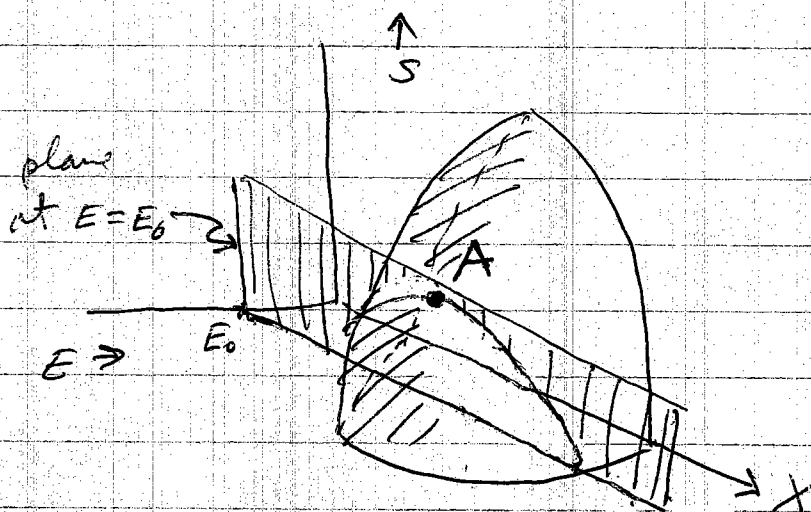
Energy minimum Principle

Postulate II stated that when constraints are removed, the equilibrium state will be the one that maximizes the entropy $S(E, V, N, \dots)$

We saw that entropy is a ^{concave} convex function of its variables



For a situation where the total E is held fixed, at value E_0 then if X is an unconstrained degree of freedom, it will take in equilibrium that value X_0 that maximizes S for the given fixed E_0 . This is determined by the intersection of the surface $S(E, X)$ with the plane at fixed $E = E_0$.



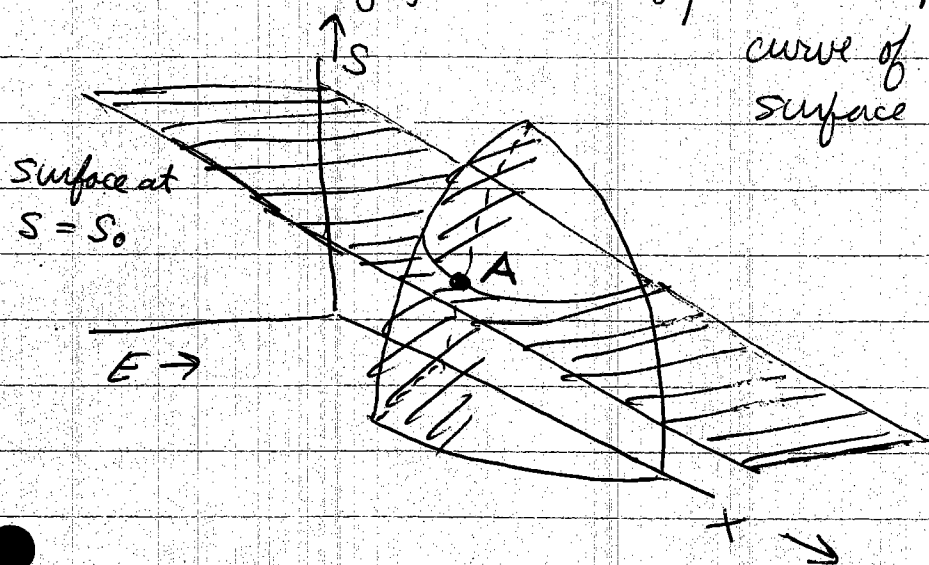
X_0 is given by the point A that maximizes S along this curve of intersection

$$S_0 = \max_X [S(E_0, X)]$$

Suppose now an alternative situation in which the total entropy S is held fixed at value S_0 .

Then if X is an unconstrained degree of freedom we see that the equilibrium state at S_0, E_0 corresponds to minimizing the energy with respect to X , along the

curve of intersection between $S(E, X)$ surface and plane of const $S = S_0$



Callen Fig 5.2

$$E_0 = \min_X [E(S_0, X)]$$

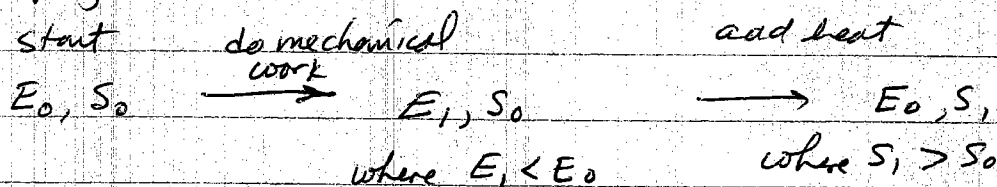
We thus have two contrasting formulations:

Entropy formulation: fundamental function is $S(E, X_1, X_2, \dots)$
 if constraint on some X_i is removed, X_i will take the value that maximizes S for the fixed total energy E . In equilib, $d^2S < 0$. S ~~convex~~ ^{concave}

Energy formulation: fundamental function is $E(S, X_1, X_2, \dots)$
 if constraint on some X_i is removed, X_i will take the value that minimizes E for the fixed total entropy S . In equilib $d^2E > 0$
 E ~~concave~~ ^{convex}

Suppose we had some equilib state for which E was not the minimum possible value for the given S ,

Then can withdraw energy from the system by doing mechanical work (for example drive a piston) while keeping S constant.



now return this energy to the system in the form of heat $E_0 - E_1 = dQ = T dS$. The energy is now back to E_0 , but the entropy has increased by $dS = (E_0 - E_1)/T$.

The system is restored to its original energy but with a higher value of entropy. But this contradicts the requirement that the original equilib state was a maximum of entropy. \Rightarrow original E had to have been the minimum.

We have now two equivalent representations

- 1) entropy $S(E, V, N)$ energy E , volume V , number N held fixed
- 2) energy $E(S, V, N)$ entropy S , volume V , number N held fixed

In certain cases it is more natural to regard temperature T as held constant, rather than S ; or to regard pressure p as held constant, rather than V ; or to regard chemical potential μ as held constant, rather than N .

We therefore wish to develop new formulations of thermodynamics that will allow us to regard T , p , or μ as a fundamental variable rather than S , V , or N . These new formulations will lead to the Helmholtz and Gibbs free energies that play the role of ~~entropy~~ ^{energy} analogous to ~~entropy~~ as the fundamental thermodynamic function of these new formulations.

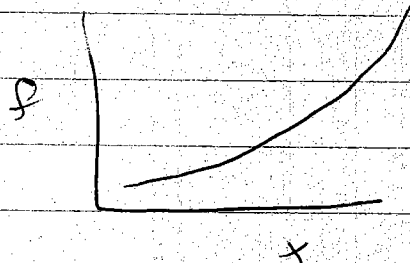
For example, we have $E(S, V, N)$ with $T = \left(\frac{\partial E}{\partial S}\right)_{V, N}$

How can we make a thermodynamic "potential" that contains all the information of $E(S, V, N)$ but depends on T rather than S .

Legendre Transformations

We treat this problem in general.

a general function $f(x)$



define the variable $p = \frac{df}{dx}$

How do we find a function that contains all the information in $f(x)$, but depends on p rather than x ?

First guess is first to invert $p(x) = \frac{df}{dx}$ to solve for x as a function of p , i.e. $x(p)$. Then one could substitute this into $f(x)$ to get

$$g(p) = f(x(p))$$

This does not have the complete information contained in $f(x)$!

For example: $f = ax^2 + bx + c$

$$p = \frac{df}{dx} = 2ax + b \Rightarrow x = \frac{p-b}{2a}$$

$$g(p) = f(x(p)) = a\left(\frac{p-b}{2a}\right)^2 + b\left(\frac{p-b}{2a}\right) + c$$

$$= \frac{a}{4a^2} (p^2 - 2pb + b^2) + \frac{bp}{2a} - \frac{b^2}{2a} + c$$

$$= \frac{p^2}{4a} - \frac{b}{2a}p + \frac{b^2}{4a} + \frac{bp}{2a} - \frac{b^2}{2a} + c$$

$$g(p) = \frac{p^2}{4a} - \frac{b^2}{4a} + c$$

Consider now $f'(x) = a(x-x_0)^2 + b(x-x_0) + c$

$$= ax^2 - 2axx_0 + ax_0^2 + bx - bx_0 + c$$

$$= ax^2 + b'x + c'$$

where $b' = b - 2ax_0$

$c' = c + bx_0 + ax_0^2$

$$\Rightarrow g'(p) = \frac{p^2}{4a} - \frac{b'^2}{4a} + c'$$

$$= \frac{p^2}{4a} - \frac{(b^2 - 4abx_0 + 4a^2x_0^2)}{4a} + c - bx_0 + ax_0^2$$

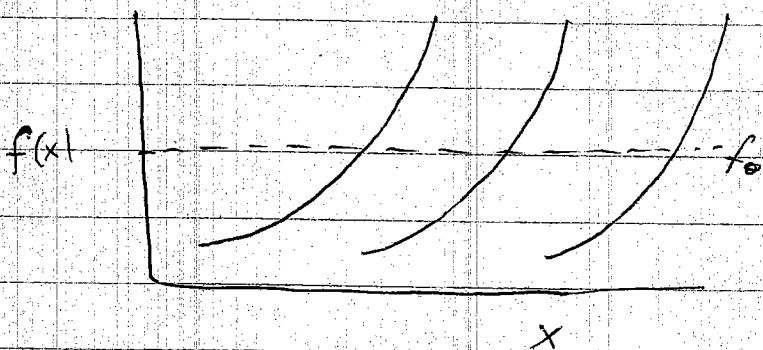
$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

$$= \frac{p^2}{4a} - \frac{b^2}{4a} + c$$

$$g'(p) = g(p)$$

clearly $g(p)$ has lost some information since we get the same $g(p)$ for $f(x)$ and $f(x-x_0)$.

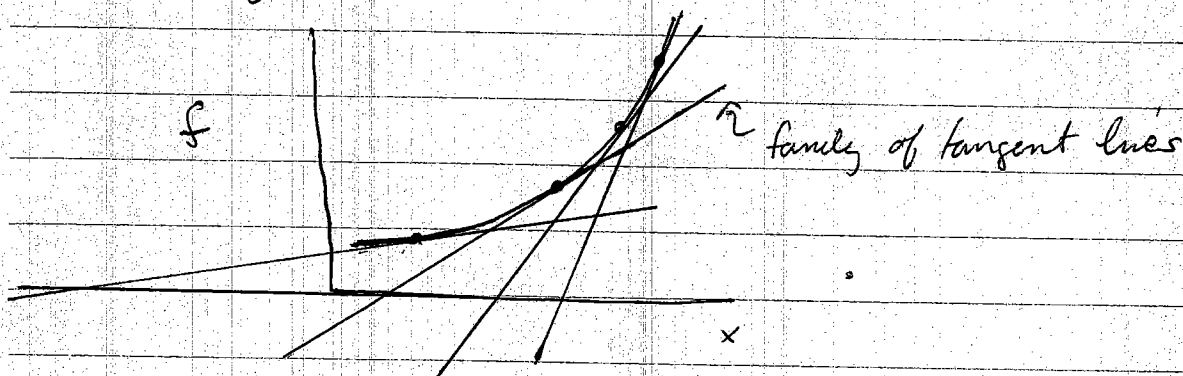
In general this is true: the procedure above cannot distinguish between $f(x)$ and $f(x-x_0)$ for any function $f(x)$.



← set of functions displaced from each other by fixed amount along x axis. For each function, the slope at constant $f = f_0$ is the same

hence writing the function as a function of the derivative $p = \frac{df}{dx}$, rather than x , results in the same $g(p)$ in each case.

However an alternate, correct, approach is given by noting that any curve can be described by the envelope of its tangent lines



the line tangent to the curve $f(x)$ at point x_0 is given by the equation

$$y = px + b \quad \text{where } p = \left. \frac{df}{dx} \right|_{x=x_0}$$

$$\text{and } f(x_0) = px_0 + b \Rightarrow b = f(x_0) - px_0$$

b is the y -intercept, i.e. $y = b$ when $x = 0$.

Define the function

$$g(p) = f(x) - px$$

$$\text{where } p = \frac{df}{dx}$$

Gives the y -intercept of the tangent to the curve at the point where the curve has slope p

In above one solves $p(x) = \frac{df}{dx}$ to get the inverse function $x(p)$, and substitutes this $x(p)$ in above expression for g to get a

function of only p .

Alternatively, one can define $g(p)$ by

$$g(p) = \underset{x}{\text{extremum}} [f(x) - px]$$

↑ take the value of x that gives an extremum of $[f(x) - px]$

In this way, $g(p)$ is independent of x , and the extremum condition guarantees that

$$\frac{df}{dx} - p = 0 \Rightarrow p = \frac{df}{dx}$$

When $f(x)$ is ~~convex~~ ^{convex}, i.e. $\frac{d^2f}{dx^2} > 0$, then the extremum is the minimum of $f - px$.

When $f(x)$ is ~~concave~~ ^{concave}, i.e. $\frac{d^2f}{dx^2} < 0$, then the extremum is the maximum of $f - px$.

Note:

$$\frac{dg}{dp} = \frac{d}{dp} [f(x) - px] = \frac{df}{dx} \frac{dx}{dp} - x - p \frac{dx}{dp}$$

$$= \left[\frac{df}{dx} - p \right] \frac{dx}{dp} - x = 0 - x$$

$$= -x$$

$$\text{since } \frac{df}{dx} = p$$

To summarize

$$f(x) \quad \phi \equiv \frac{df}{dx}$$

$$g(p) = f(x) - px \quad \Rightarrow \quad \frac{dg}{dp} = -x$$

One says that $g(p)$ is the Legendre transform of $f(x)$ and that x and p are conjugate variables.

$g(p)$ contains all the information that $f(x)$ does, i.e. if one knows $g(p)$ then one can construct $f(x)$ from it, by constructing all the tangent lines $y = px + g(p)$. The Legendre transform allows one to switch variables from x to $\frac{df}{dx}$ without losing information.

You may have already seen Legendre transforms in classical mechanics. In the Lagrange formulation, the fundamental function is the Lagrangian $\mathcal{L}[q, \dot{q}]$ which depends on the variables q and \dot{q} . In the Hamilton formulation one wants to replace the variable \dot{q} by the variable $\phi \equiv \frac{\partial \mathcal{L}}{\partial \dot{q}}$. The fundamental function to use,

which is a function of q and ϕ rather than q and \dot{q} , is therefore the Legendre transform of the Lagrangian

$$\mathcal{L}[q, \dot{q}] - \phi \dot{q} = -\mathcal{H}[p, q]$$

where \mathcal{H} is the Hamiltonian. Because ϕ and q are conjugate variables, we know that

$$\frac{\partial (-\mathcal{H})}{\partial \dot{p}} = -\dot{q} \quad \text{or} \quad \frac{\partial \mathcal{H}}{\partial \dot{p}} = \dot{q}$$

which is one of the Hamilton dynamic equations (the other is $\frac{\partial \mathcal{H}}{\partial q} = -\dot{p}$)

Legendre transform and Thermodynamics

Helmholtz Free Energy $A(T, V, N)$

If we want a formulation of thermodynamics in which temperature T rather than entropy S is regarded as an independent variable, we take the Legendre transform of the energy

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

$$\Rightarrow A(T, V, N) \equiv E - TS$$

Helmholtz Free Energy
sometimes written as $F(T, V, N)$

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

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

$$\left(\frac{\partial E}{\partial N} \right)_{S, \mu}$$

$$dA = \left(\frac{\partial A}{\partial T} \right)_{V, N} dT + \left(\frac{\partial A}{\partial V} \right)_{T, N} dV + \left(\frac{\partial A}{\partial N} \right)_{T, V} dN$$

$$\Rightarrow dA = -SdT - pdV + \mu dN$$

Since $E = TS - pV + \mu N$, $A = E - TS = -pV + \mu N$

$$A = -pV + \mu N$$

checking the derivatives more carefully

$A = E - TS$ to take Legendre transform wrt in
principal conjugate $T(S, V, N) = \left(\frac{\partial E}{\partial S}\right)_{N, V}$
and invert it to get $S(T, V, N)$
then substitute into the above

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

then

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

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

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

Similarly

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

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

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

Similarly

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