

Summary

The fundamental thermodynamic function, which determines all thermodynamic behavior, is the entropy

$S(E, V, N)$ as function of the extensive variables
 E, V, N

or equivalently the total internal energy

$E(S, V, N)$ as function of the extensive variable
 S, V, N

The partial derivatives

$$\left. \begin{aligned} \left(\frac{\partial E}{\partial S}\right)_{V, N} &= T(S, V, N) \\ -\left(\frac{\partial E}{\partial V}\right)_{S, N} &= p(S, V, N) \\ \left(\frac{\partial E}{\partial N}\right)_{S, V} &= \mu(S, V, N) \end{aligned} \right\} \begin{array}{l} \text{give the three} \\ \text{"equations of state"} \end{array}$$

If one knows the three equations of state, then it is equivalent to knowing the fundamental thermodynamic function since by Euler's relation

$$E = TS - pV + \mu N$$

If one knows any two of the equations of state one can find the third by using the Gibbs-Duhem relation

$$N d\mu = -SdT + Vdp$$

example: The ideal monatomic gas

$$\text{From expt: } PV = Nk_B T \quad \Rightarrow \quad \frac{P}{T} = \frac{N}{V} k_B = \frac{k_B}{v}$$
$$E = \frac{3}{2} Nk_B T \quad \Rightarrow \quad \frac{1}{T} = \frac{3}{2} k_B \frac{N}{E} = \frac{3}{2} \frac{k_B}{u}$$

if we can find μ , then we have entropy S via

$$S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N$$

From Gibbs-Duhem relation in entropy representation

$$d\left(\frac{\mu}{T}\right) = u d\left(\frac{1}{T}\right) + v d\left(\frac{P}{T}\right)$$

$$= u \frac{3}{2} k_B d\left(\frac{1}{u}\right) + v k_B d\left(\frac{1}{v}\right)$$

$$d\left(\frac{\mu}{T}\right) = -\frac{3}{2} \frac{k_B}{u} du - \frac{k_B}{v} dv$$

integrate to get

$$\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -\frac{3}{2} k_B \ln\left(\frac{u}{u_0}\right) - k_B \ln\left(\frac{v}{v_0}\right)$$

where u_0 and v_0 are some reference state, and $\left(\frac{\mu}{T}\right)_0$ is an unknown constant of integration. Then one gets

$$S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N = \frac{3}{2} \frac{k_B E}{(E/N)} + \frac{k_B V}{(V/N)}$$

$$+ \frac{3}{2} Nk_B \ln\left(\frac{u}{u_0}\right) + k_B N \ln\left(\frac{v}{v_0}\right) \Rightarrow \left(\frac{\mu}{T}\right)_0 N$$

$$S = \frac{3}{2} k_B N + k_B N \left(\frac{\mu}{T}\right)_0 + Nk_B \ln\left[\left(\frac{u}{u_0}\right)^{3/2} \left(\frac{v}{v_0}\right)\right]$$

use

$$E = uN, E_0 \equiv u_0 N_0, V = vN, V_0 \equiv v_0 N_0$$

$$\Rightarrow S(E, V, N) = \frac{N}{N_0} S_0 + N k_B \ln \left[\left(\frac{E}{E_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \left(\frac{N}{N_0} \right)^{-5/2} \right]$$

where $S_0 = \frac{5}{2} k_B N_0 \ln \left(\frac{\mu}{T} \right)_0 N_0$ is a constant

So from experimental knowledge of two of the equations of state $\frac{1}{T}$ and $\frac{P}{T}$ as functions of E, N, V , we have derived the entropy $S(E, V, N)$. All behaviors of the ideal gas can now be deduced from knowledge of S .

Alternatively, we could derive $a = \frac{S}{N}$ as follows:

$$E = TS - PV + \mu N \Rightarrow S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N$$

$$\Rightarrow a = \frac{u}{T} + \frac{P}{T} v - \frac{\mu}{T} \quad \text{where } u = \frac{E}{N}, v = \frac{V}{N}$$

$$da = \frac{1}{T} du + \frac{P}{T} dv + \underbrace{u d\left(\frac{1}{T}\right) + v d\left(\frac{P}{T}\right) - d\left(\frac{\mu}{T}\right)}_{\text{these cancel due to the Gibbs-Duhem relation as expressed in the entropy formulation}}$$

So

$$\Rightarrow da = \frac{1}{T} du + \frac{P}{T} dv$$

$$ds = \frac{1}{T} du + \frac{p}{T} dv$$

$$= \frac{3}{2} \frac{k_B}{u} du + \frac{k_B}{v} dv \quad \text{since } \int \frac{1}{T} = \frac{3}{2} \frac{k_B}{u}$$

integrate

$$\left\{ \begin{array}{l} \frac{p}{T} = \frac{k_B}{v} \end{array} \right.$$

$$s - s_0 = \frac{3}{2} k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

$$s = s_0 + k_B \ln \left[\left(\frac{u}{u_0} \right)^{3/2} \left(\frac{v}{v_0} \right) \right]$$

substitute in $S = Ns$, $E = Nu$, $V = Nv$

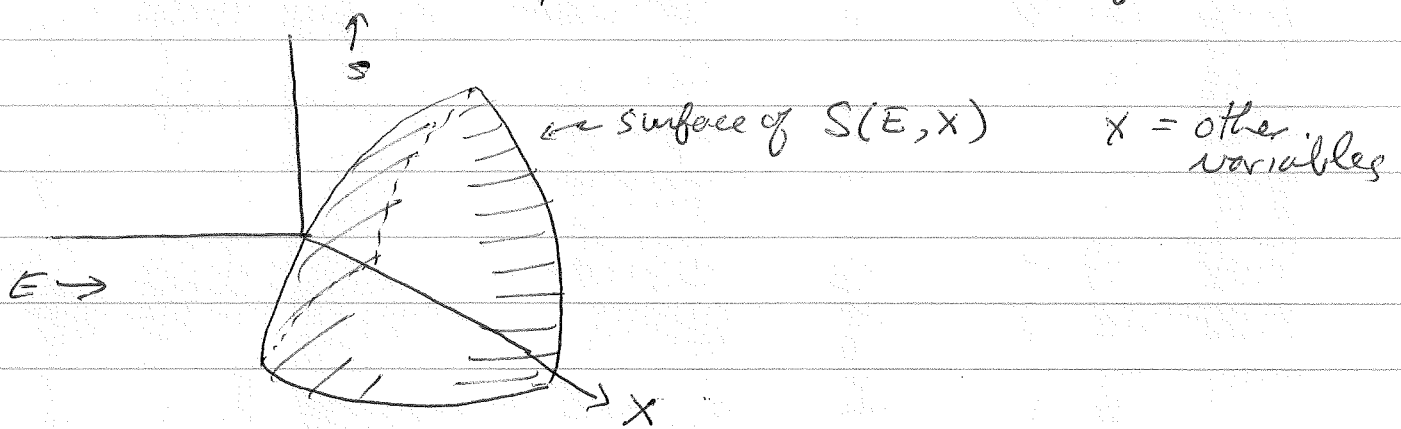
$$S_0 = N_0 s_0, \quad E_0 = N_0 u_0, \quad V_0 = N_0 v_0$$

and we recover the earlier result for $S(E, V, N)$

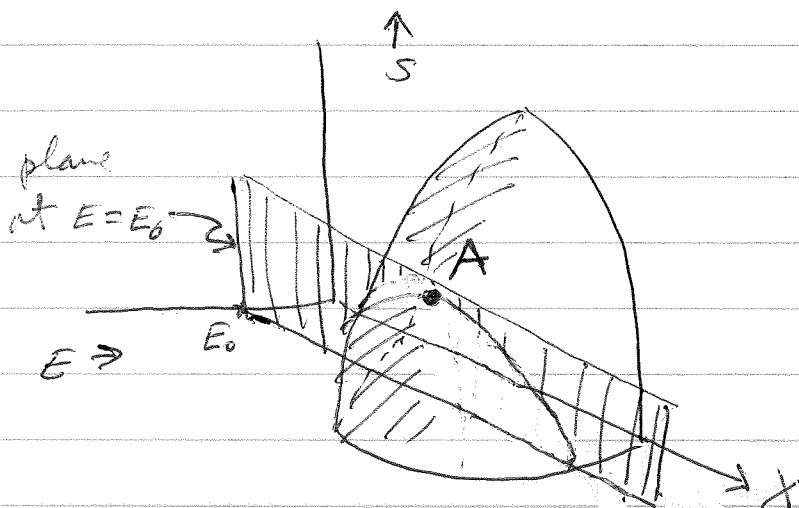
Energy Minimum Principle

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 ~~convex~~ ^{concave} 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 $E = E_0$.



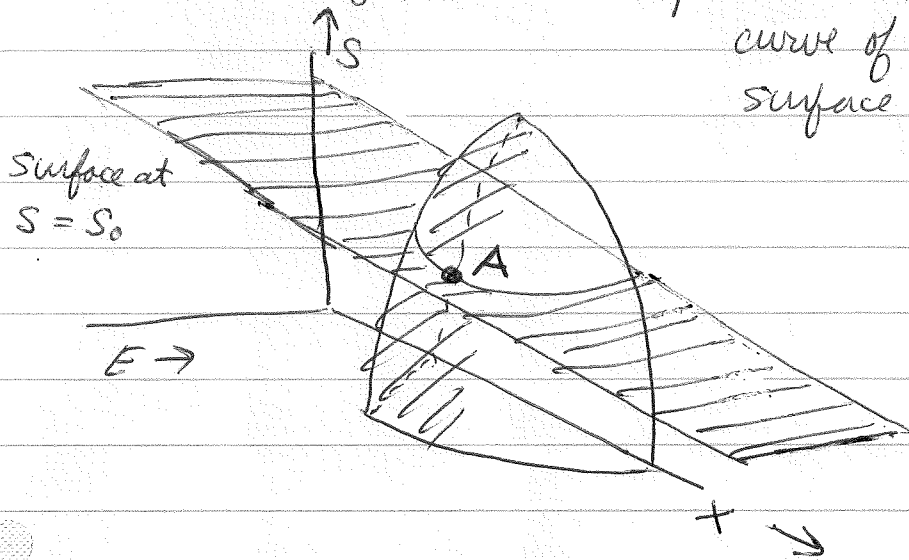
X_0 is given by the point A that maximizes S along this curve of intersection

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

Callen Fig 5.1

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 ^① doing mechanical work (for example drive a piston) while keeping S constant.

start E_0, S_0 $\xrightarrow[\text{work}]{\text{do mechanical } \textcircled{1}}$ E_1, S_0 $\xrightarrow{\text{add heat } \textcircled{2}}$ E_0, S_1
where $E_1 < E_0$ where $S_1 > S_0$

^② 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~~ analogous to energy as the fundamental thermodynamic function of these new formulations.

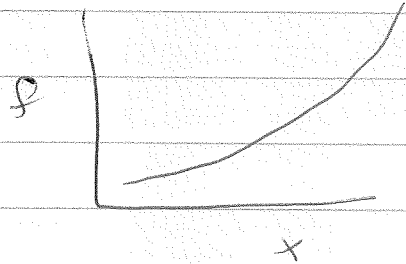
For example, we have $E(S, V, N)$ with $T = \left(\frac{\partial E}{\partial S}\right)_{V, N}$

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 just 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 $b' = b - 2ax_0$

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

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

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

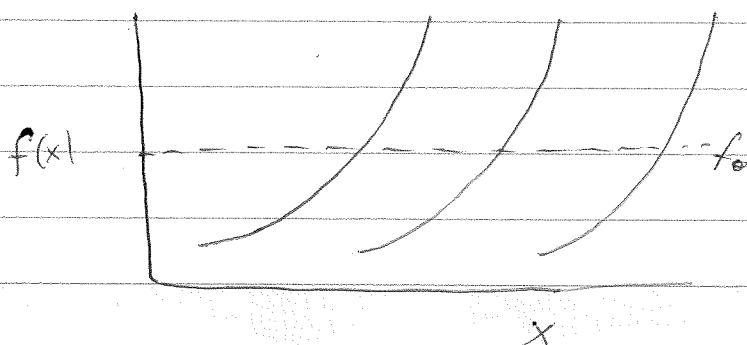
$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$

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

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

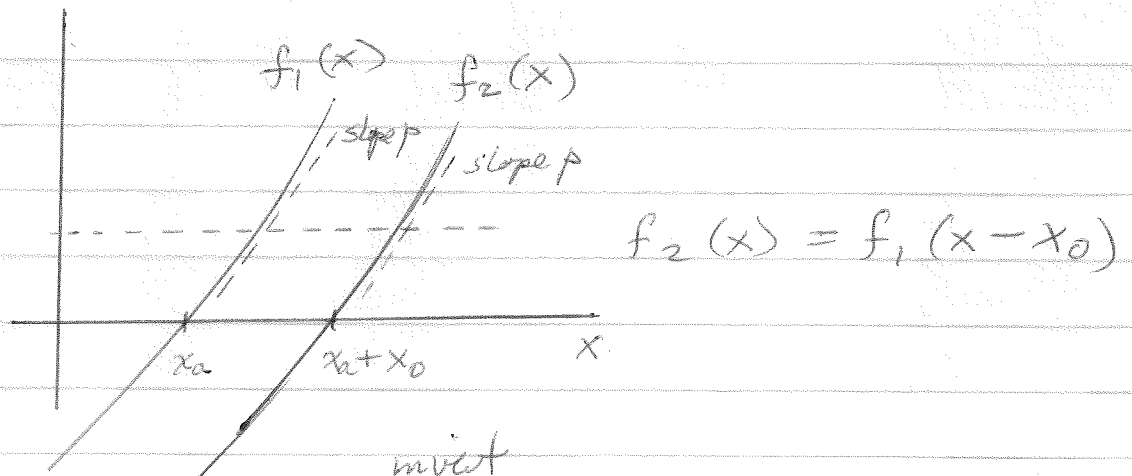
clearly $g(p)$ has lost some information since we get the same $g(p)$ for $f(x)$ and $f(x-x_0)$.

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

Consider $f_1(x)$ and $f_2(x)$ defined as follows,



$$\text{Define } p_1(x) = \frac{df_1(x)}{dx} \xrightarrow{\text{invert}} x_1(p)$$

$$p_2(x) = \frac{df_2(x)}{dx} \xrightarrow{\text{invert}} x_2(p)$$

$$\frac{df_1(x-x_0)}{dx} = p_1(x-x_0)$$

$$\Rightarrow x_2(p) = x_1(p) + x_0$$

i.e. If $f_1(x)$ has slope p at x_1 , then $f_2(x)$ has slope p at $x_2 = x_1 + x_0$

$$g_1(p) = f_1(x_1(p))$$

$$g_2(p) = f_2(x_2(p)) = f_1(x_2(p) - x_0)$$

$$= f_1(x_1(p) + x_0 - x_0) = f_1(x_1(p))$$

$$= g_1(p)$$

So given $g(p) = g_1 = g_2$, we cannot tell if the original function was f_1 or f_2 ! So $g(p)$ does NOT have all the same information as the function $f(x)$.