T, p, μ are really functions of only <u>two</u> <u>intensive</u> variables $s = S/N$ and $v = V/N$

Since the three variables T, p, μ are all functions of the two variables s, v, there must exist a relation among them – T, p, μ are <u>not independent</u>.

For example, one could imagine taking the two equations $T = T(s, v)$ and $p = p(s, v)$ and solving for s and v in terms of T and p. One could then take this result and substitute it into the third equation $\mu = \mu(s, v)$ to get a relation $\mu = \mu(T, p)$.

The differential form for this constraint on T, p, μ is known as the <u>Gibbs-Duhem</u> relation. We derive it as follows:

<u>Consider</u>:

$$\lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N)$$

differentiate with respect to λ

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

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

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

$$\Rightarrow E(S,V,N) = T(\lambda S,\lambda V,\lambda N)\, S - p(\lambda S,\lambda V,\lambda N)\, V + \mu(\lambda S,\lambda V,\lambda N)\, N$$

Now take $\lambda = 1$,

$$E(S,V,N) = T(S,V,N)\, S - p(S,V,N)\, V + \mu(S,V,N)\, N$$

$$(*) \quad \boxed{E = TS - pV + \mu N} \qquad \text{Euler relation}$$

or dividing by N

$$u = Ts - pv + \mu$$

Now from the fundamental definitions of T, p, μ we can write

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN$$

$$\Rightarrow dE = T\,dS - p\,dV + \mu\,dN$$

But from $(*)$ above we can write

$$dE = T\,dS + S\,dT - p\,dV - V\,dp + \mu\,dN + N\,d\mu$$

Subtracting these two differential relations gives

$$\boxed{\begin{aligned} &S\,dT - V\,dp + N\,d\mu = 0 \\ \text{or} \quad &d\mu = -s\,dT + v\,dp \end{aligned}} \qquad \text{Gibbs-Duhem relation}$$

one cannot vary T, p, and μ independently.
The Gibbs - Duhem relation gives the variation of one in terms of the variation in the other two.

We can also derive a Gibbs - Duhem relation in the entropy formulation:

$$S = \frac{E}{T} + \frac{p}{T}V - \frac{\mu}{T}N \qquad \text{from Euler relation}$$

$$\Rightarrow dS = E\,d\left(\frac{1}{T}\right) + \frac{1}{T}dE + V\,d\left(\frac{p}{T}\right) + \frac{p}{T}dV - N\,d\left(\frac{\mu}{T}\right) - \frac{\mu}{T}dN$$

but from definitions $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$, $\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T}$, $\left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{-\mu}{T}$
we get

$$dS = \left(\frac{1}{T}\right)dE + \left(\frac{p}{T}\right)dV - \left(\frac{\mu}{T}\right)dN$$

combining with the above we get

$$E\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{p}{T}\right) - N\,d\left(\frac{\mu}{T}\right) = 0$$

$$\text{or} \quad d\left(\frac{\mu}{T}\right) = u\,d\left(\frac{1}{T}\right) + v\,d\left(\frac{p}{T}\right)$$

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 variables S, V, N

The partial derivatives

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

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 example: The ideal monatomic gas

From expt:

$$PV = Nk_BT \Rightarrow \frac{P}{T} = \frac{N}{V}k_B = \frac{k_B}{v}$$

$$E = \frac{3}{2}Nk_BT \Rightarrow \frac{1}{T} = \frac{3}{2}k_B\frac{N}{E} = \frac{3}{2}\frac{k_B}{u}$$

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

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

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

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

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

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

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

So from experimental knowledge of two of the equations of state $\frac{1}{T}$ ad $\frac{p}{T}$ 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 $s = \frac{S}{N}$ as follows:

$$E = TS - pV + \mu N \quad \Rightarrow \quad S = \frac{E}{T} + \frac{p}{T} V - \frac{\mu}{T} N$$

$$\Rightarrow s = \frac{u}{T} + \frac{p}{T} v - \frac{\mu}{T} \qquad \text{where } u = \frac{E}{N},\ v = \frac{V}{N}$$

$$ds = \frac{1}{T} du + \frac{p}{T} dv + \underbrace{u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{p}{T}\right) - d\left(\frac{\mu}{T}\right)}$$

these cancell due to the Gibbs-Duhem relation as expressed in the entropy formulation

So

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

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

$$= \frac{3}{2}\frac{k_B}{u}\,du + \frac{k_B}{v}\,dv \qquad \text{since} \begin{cases} \frac{1}{T} = \frac{3}{2}\frac{k_B}{u} \\ \frac{p}{T} = \frac{k_B}{v} \end{cases}$$

integrate

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

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

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

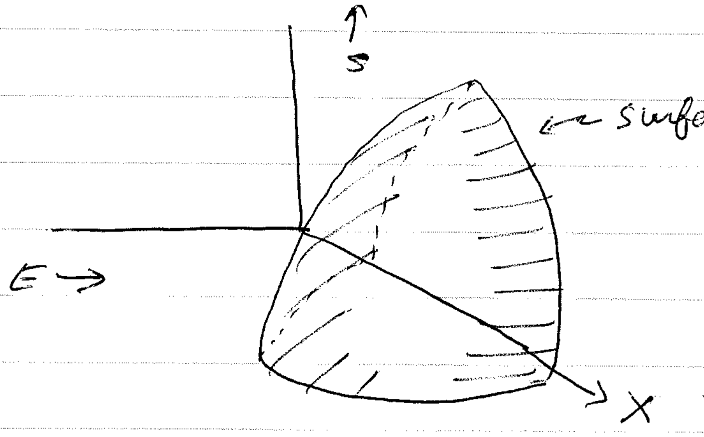
$S_0 = N_0 s_0$, $E_0 = N_0 u_0$, $V_0 = N_0 v_0$

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

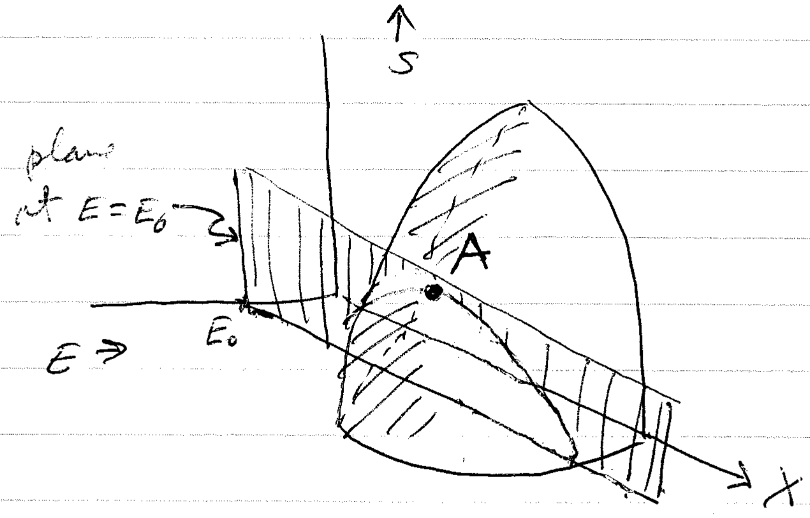
Energy Minimum Principle

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

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 equilib 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 $E = E_0$

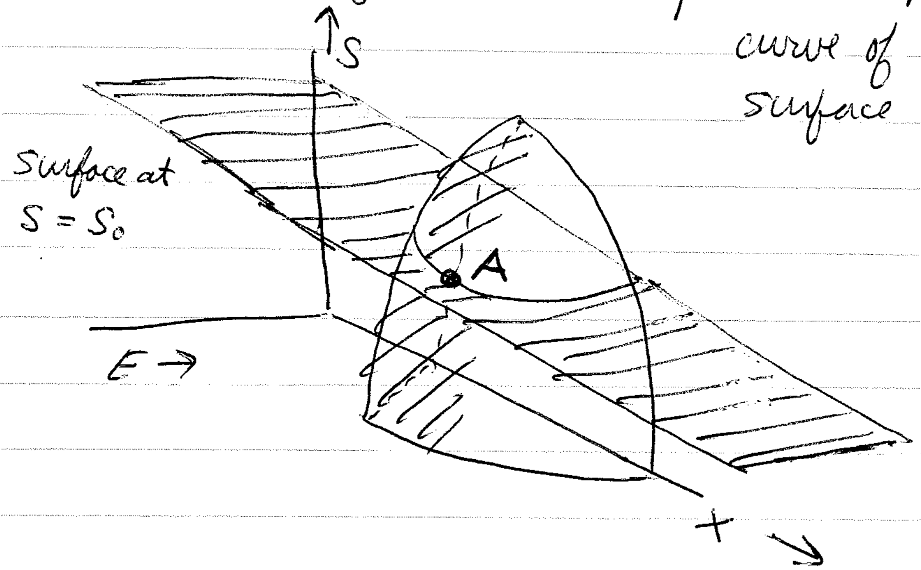


X_0 is given by the point A that maximizes S along this curve of intersection

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

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

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

We thus have two contrasting formulations:

<u>entropy formulation</u>: 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

<u>energy formulation</u>: 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.

$$\overset{\text{start}}{E_0, S_0} \xrightarrow{\text{do mechanical work}} \underset{\text{where } E_1 < E_0}{E_1, S_0} \xrightarrow{\text{add heat}} \underset{\text{where } S_1 > S_0}{E_0, S_1}$$

now return this energy to the system in the form of heat $E_0 - E_1 = dQ = TdS$. 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 max min 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.

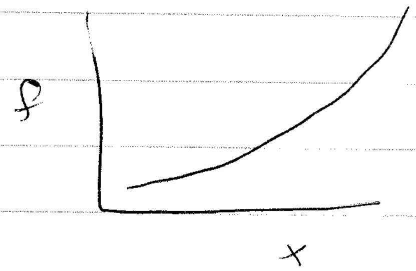
We therefore wish to develop new formulations of thermodynamics that will allow us to regard T, p, or μ as a fundamental variable rather than S, V, or N. These new formulations will lead to the Helmholtz and Gibb free energies that play the role ~~of entropy~~ analogues to ~~entropy~~ energy as the fundamental 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 $p \equiv \frac{df}{dx}$

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 $p(x) \equiv \frac{df}{dx}$ to solve for x as a function of p, ie $x(p)$. 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: $f = ax^2 + bx + c$.

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

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

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

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

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

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 $b' = b - 2ax_0$

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

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

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

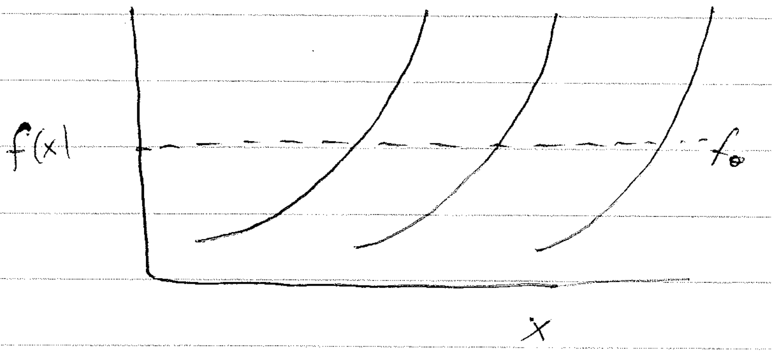
$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

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

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

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

<u>In general</u> 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