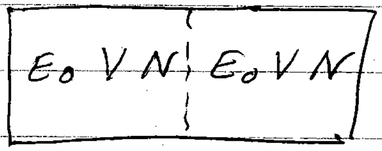
~~Convexity~~ Concavity of the Entropy

Callen Chpt 3 + 5

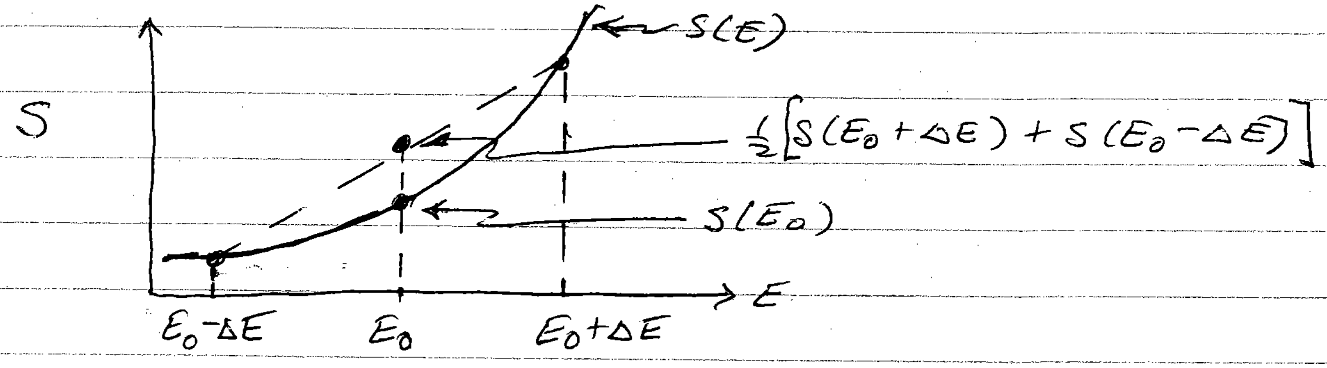


consider a container of gas conceptually divide into two equal halves (no physical wall)

If N and V are fixed to be the same on both sides, we expect the energy will be equal on both sides

$$S^{total} = S(2E_0, 2V, 2N) = S(E_0, V, N) + S(E_0, V, N)$$

Consider ~~how~~ S depends on E. If S were <u>not</u> a ~~convex~~ concave function of E (ie if $\partial^2 S/\partial E^2 > 0$) then the system would be unstable as follows:



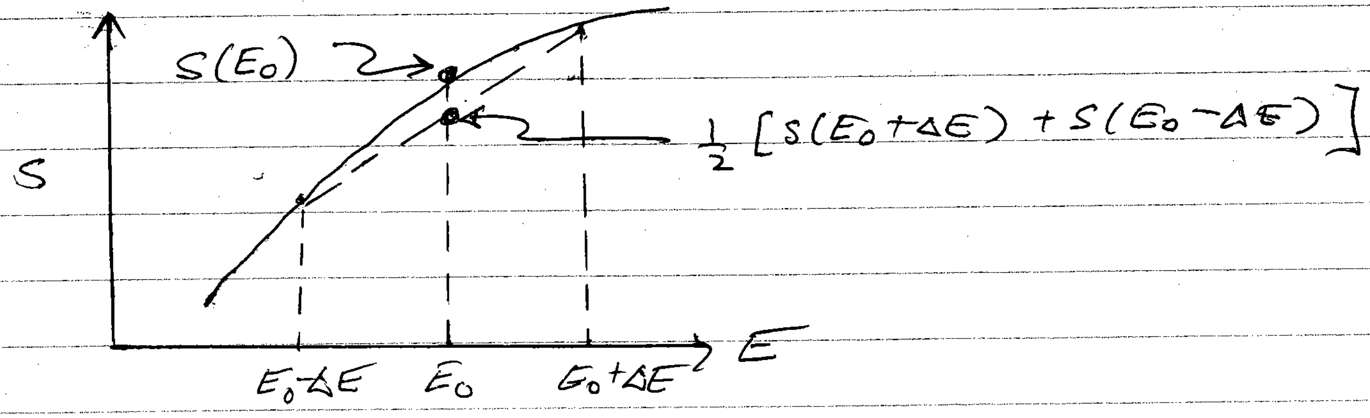
If $S(E)$ is not ~~convex~~ concave, then we have from above

$$2S(E_0) < S(E_0+\Delta E) + S(E_0-\Delta E)$$

Therefore, the total system would <u>increase</u> its entropy by having the LHS with $E_0 - \Delta E$, and the RHS with $E_0 + \Delta E$ — the system would not be stable with equal energies on both sides!

Since, by Postulate II, the systems acts so as to maximize its entropy, we see that the system will be unstable if $S(E)$ is not ~~convex~~ concave.

If $S(E)$ is ~~convex~~ concave, ie $\frac{\partial^2 S}{\partial E^2} < 0$, this does not happen



Now $2S(E_0) > S(E_0+\Delta E) + S(E_0-\Delta E)$

The maximum total entropy S^{total} will be when both halves have equal energy E_0

$\Rightarrow$ $S(E)$ is ~~convex~~ concave

By similar arguement, S must be a ~~convex~~ concave function of *all* its variables.

$d^2S < 0$ ~~convex~~ concave

Further consequences of S being a 1st order homogeneous function

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

$$\Rightarrow \quad \lambda E(S,V,N) = E(\lambda S, \lambda V, \lambda N)$$ E is also a 1st order homogeneous function

differentiate with respect to S.

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

$$\Rightarrow \quad \lambda\, T(S,V,N) = T(\lambda S, \lambda V, \lambda N)\, \lambda$$

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

similarly from $p = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$ and $\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$ we conclude

$$\left.\begin{aligned} T(S,V,N) &= T(\lambda S, \lambda V, \lambda N) \\ p(S,V,N) &= p(\lambda S, \lambda V, \lambda N) \\ \mu(S,V,N) &= \mu(\lambda S, \lambda V, \lambda N) \end{aligned}\right\}$$

T, p, μ are homogeneous functions of zeroth order

let $\lambda = \frac{1}{N}$, then

$$\left.\begin{aligned} T(S,V,N) &= T\left(\tfrac{S}{N}, \tfrac{V}{N}, 1\right) = T(s,v) \\ P(S,V,N) &= P\left(\tfrac{S}{N}, \tfrac{V}{N}, 1\right) = P(s,v) \\ \mu(S,V,N) &= \mu\left(\tfrac{S}{N}, \tfrac{V}{N}, 1\right) = \mu(s,v) \end{aligned}\right\}$$ "equations of state

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

Since the three variables T, p, μ are all functions of the two variables u, v, there must exist a relation among them — T, p, μ are *not independent*.

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 *Gibbs-Duhem* relation. We derive it as follows:

Consider:

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

differentiate with respect to λ

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where $S_0 = \frac{5}{2} k_B N_0 + \left(\frac{\mu}{T_0}\right) N_0$ a constant

fundamental equation, expresses S in terms of E, V, N

alternatively

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

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

$$= \frac{3}{2}\frac{k_B}{u} du + \frac{k_B}{v} dv$$

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

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

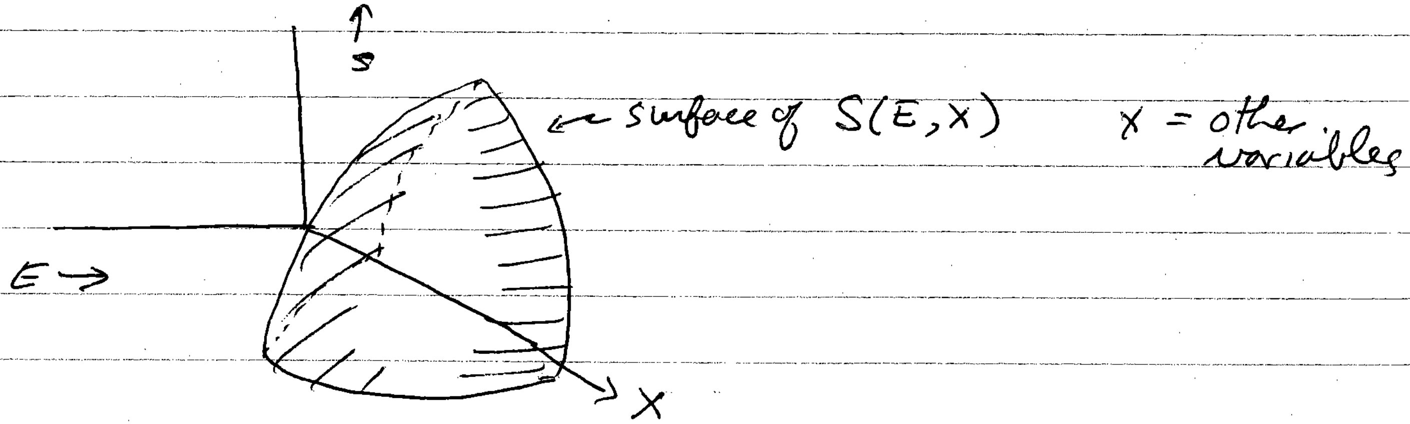
$$s = s_0 + k_B \ln\left[\left(\frac{u}{u_0}\right)^{3/2}\left(\frac{v}{v_0}\right)\right]$$ same as above

fundamental equation, expresses s in terms of u and v

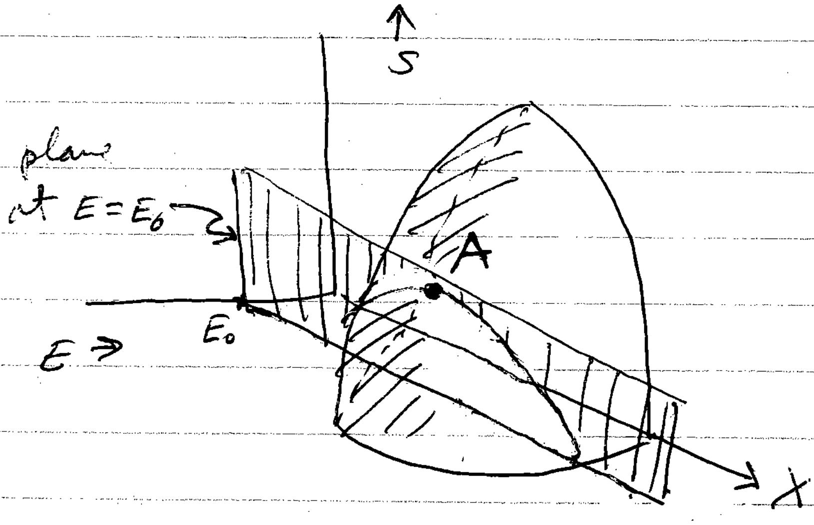
Energy Minimum Principle

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 $E = E_0$

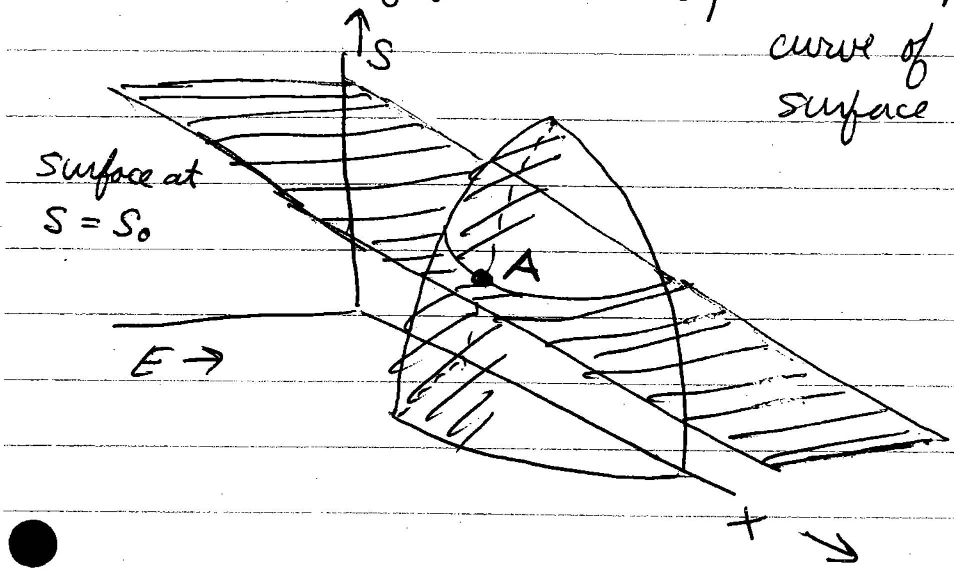


X_0 is given by the point A that maximizes S along this curve of intersection

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

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:

entropy formulation: fundamental function is $S(E, X_1, X_2, \ldots)$
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, $d^2 S < 0$. S ~~convex~~ concave

energy formulation: fundamental function is $E(S, X_1, X_2, \ldots$
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 $d^2 E > 0$
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.

$$\text{start} \quad E_0, S_0 \xrightarrow[\text{work}]{\text{do mechanical}} E_1, S_0 \xrightarrow{\text{add heat}} E_0, S_1$$

$$\text{where } E_1 < E_0 \qquad \text{where } S_1 > S_0$$

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.