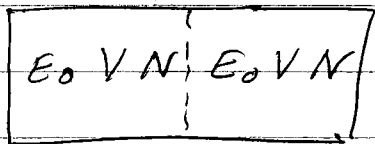Concavity

~~Convexity~~ of the Entropy   Callen Chpt 3 + 5
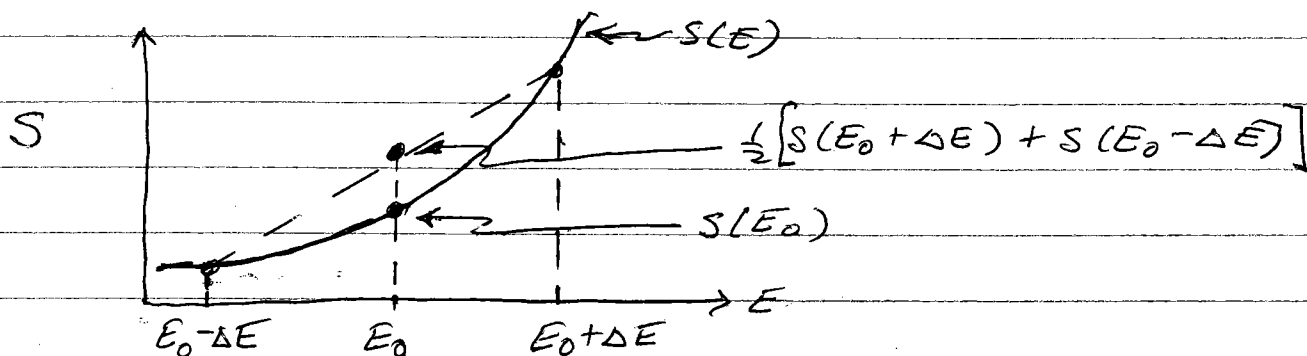
consider a container of gas conceptually divide into two equal halves (no physical wall)

$$E_0 \; V \; N \; | \; E_0 \; V \; N$$

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 not 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 increase 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
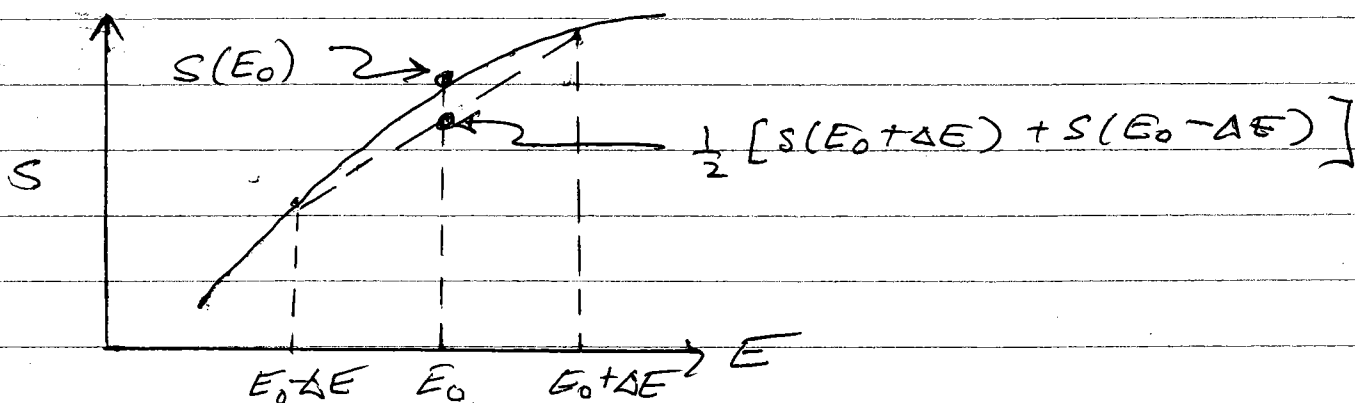
Now $2S(E_0) > S(E_0 + \Delta E) + S(E_0 - \Delta E)$

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

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

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

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

Further consequences of S being a 1st order homogeneous function

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

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

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

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

T, p, μ are homogeneous functions of __zeroth__ order

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

$$T(S, V, N) = T\left(\frac{S}{N}, \frac{V}{N}, 1\right) = T(s, v) \quad \left.\begin{array}{c} \text{equation} \\ \text{of state} \end{array}\right.$$
$$P(S, V, N) = P\left(\frac{S}{N}, \frac{V}{N}, 1\right) = P(s, v)$$
$$\mu(S, V, N) = \mu\left(\frac{S}{N}, \frac{V}{N}, 1\right) = \mu(s, v)$$

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

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

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

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

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

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

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

or dividing by N

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

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

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

$$\Rightarrow dE = TdS - pdV + \mu dN$$

But from (*) above we can write

$$dE = TdS + SdT - pdV - Vdp + \mu dN - Nd\mu$$

Subtracting these two differential relations gives

$$\boxed{\begin{array}{l} SdT - Vdp + Nd\mu = 0 \\[2mm] \text{or} \quad d\mu = -sdT + vdp \end{array}}$$

$\underline{\text{Gibbs - Duhem}}$
$\underline{\text{relation}}$

one cannot vary T, P, and μ <u>independently</u>.
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 $\quad d\left(\frac{\mu}{T}\right) = u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right)$

example : The ideal monatomic gas

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

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

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

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

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

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

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

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

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

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

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

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

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

$$s = s_0 + k_B \ln \left[\left(\frac{u}{u_0} \right)^{3/2} \left(\frac{v}{v_0} \right) \right] \quad \text{same as above}$$
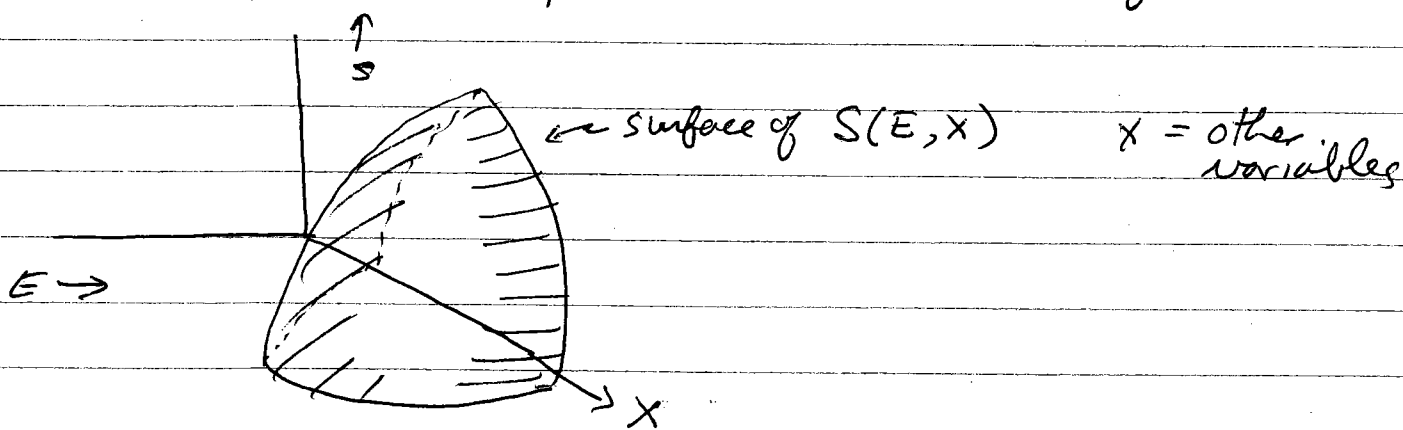
fundamental equation, expresses s in terms of u and v

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

← surface of $S(E, X)$ X = other 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 $E = E_0$
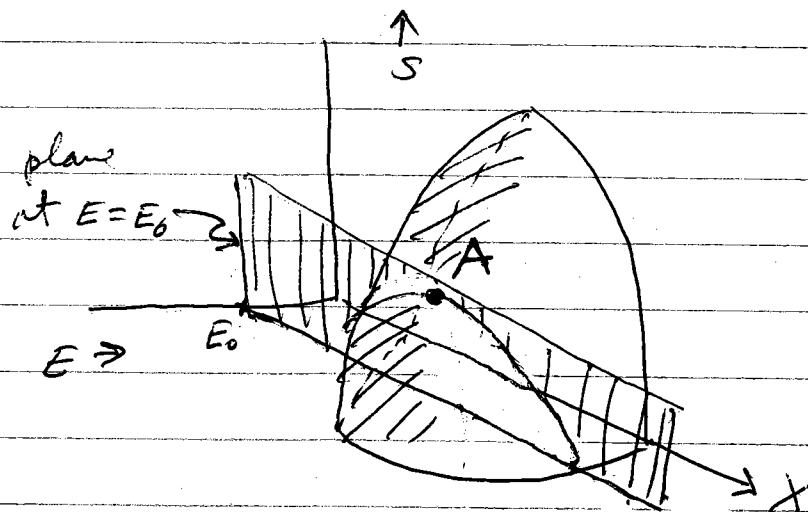
X_0 is given by the point A that maximizes S along this curve of intersection

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

plane at $E = E_0$

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 $S = S_0$

surface at $S = S_0$
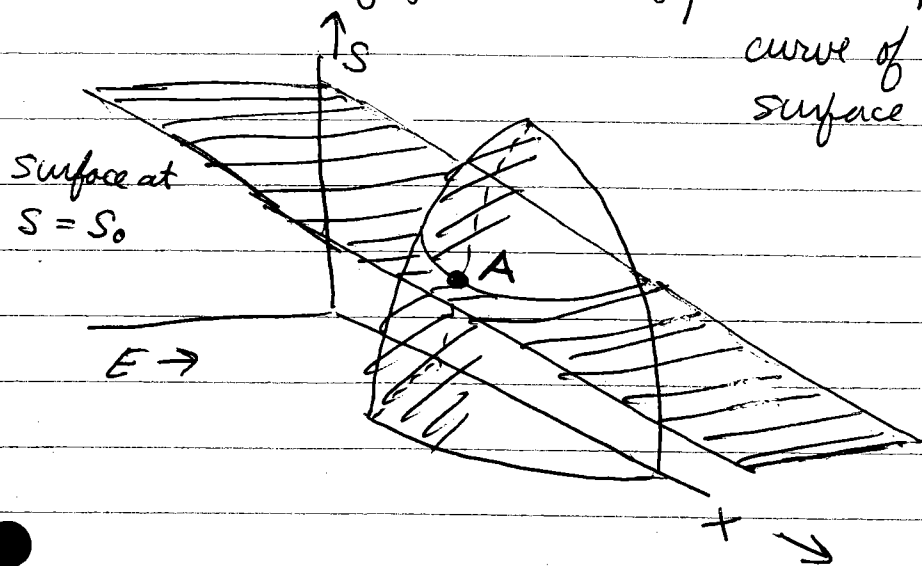
Callen Fig 5.2

$$E_0 = \min_{X}\left[E(S_0, X)\right]$$

We thus have two contrasting formulations:

entropy formulation: fundamental function is $S(E, X_1, X_2, \dots)$ 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