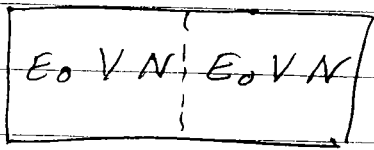


Concavity

Concavity of the Entropy

Callen Chpt 3 + 5

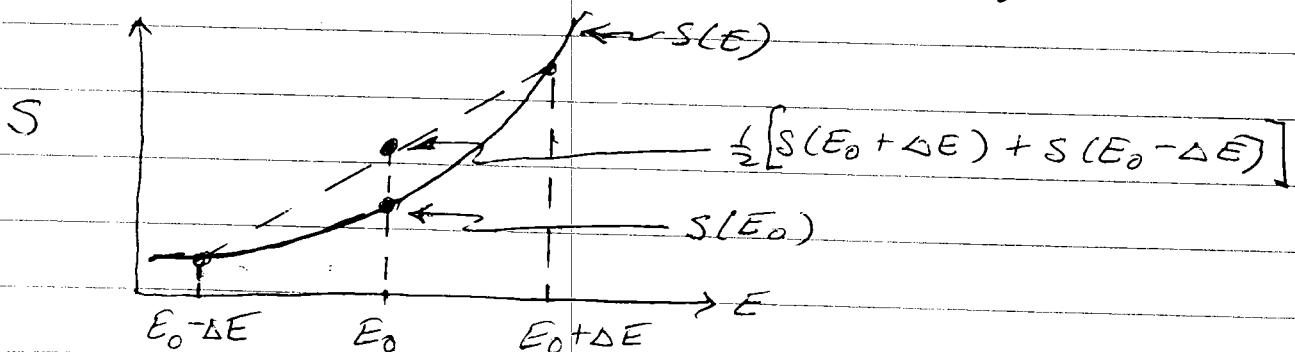


consider a container of gas
conceptually divide into two
equal halves (no physical wall)

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

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

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



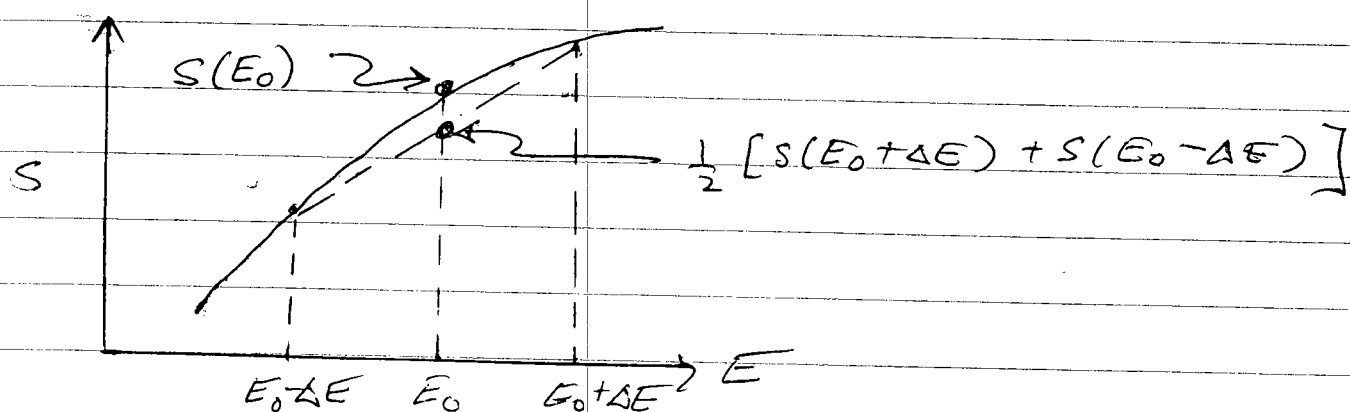
If $S(E)$ is not convex, then we have from above

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

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 system 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}, i.e. $\frac{\partial^2 S}{\partial E^2} < 0$, 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

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

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

differentiate with respect to S .

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

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

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

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

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

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

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

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

or dividing by N

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

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

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

Subtracting these two differential relations gives

$$\boxed{SdT - Vdp + Nd\mu = 0}$$

or

$$\boxed{d\mu = -s dT + v dp}$$

Gibbs-Duhem
relation

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

$$\begin{aligned} E(S, V, N) &= \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \right)_{\lambda V, \lambda N} \left(\frac{\partial(\lambda S)}{\partial \lambda} \right) \\ &+ \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \right)_{\lambda S, \lambda N} \left(\frac{\partial(\lambda V)}{\partial \lambda} \right) \\ &+ \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \right) \left(\frac{\partial(\lambda N)}{\partial \lambda} \right) \end{aligned}$$

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:

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

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

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

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

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

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 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

example: The ideal monatomic gas

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

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

$$S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N = \frac{3}{2} \frac{k_B E}{(E/N)} + \frac{k_B V}{(V/N)}$$
$$+ \frac{3}{2} N k_B \ln\left(\frac{u}{u_0}\right) + k_B N \ln\left(\frac{v}{v_0}\right) + \left(\frac{\mu}{T}\right)_0 N$$

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

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

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

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

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

$$\Rightarrow d\mathcal{Q} = \frac{1}{T} du + \frac{P}{T} dv$$

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

$$\mathcal{Q} - \mathcal{Q}_0 = \frac{3}{2} k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

$$\mathcal{Q} = \mathcal{Q}_0 + \frac{3}{2} k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

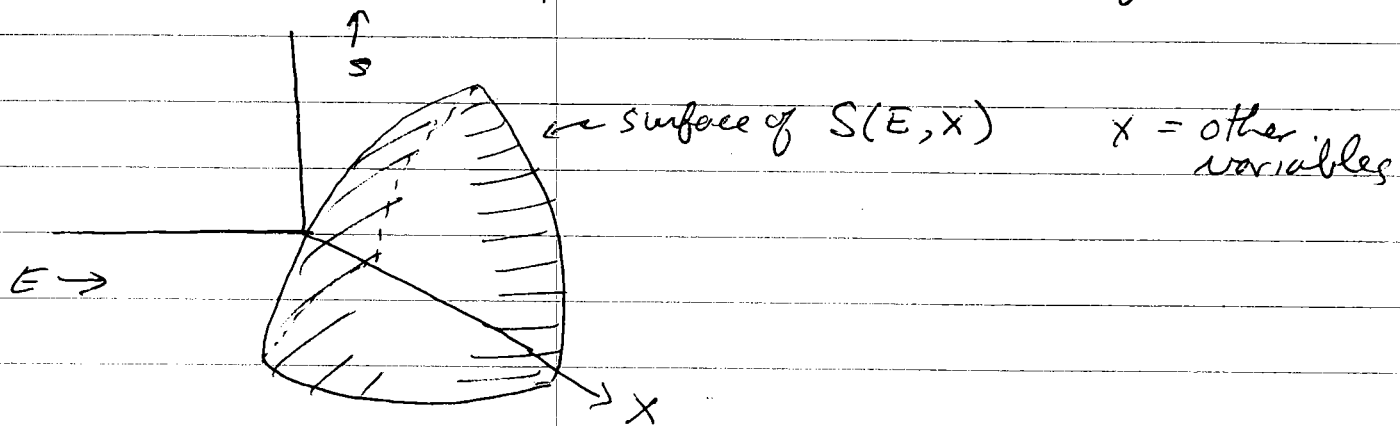
$$\mathcal{Q} = \mathcal{Q}_0 + k_B \ln \left[\left(\frac{u}{u_0} \right)^{3/2} \left(\frac{v}{v_0} \right) \right] \text{ same as above}$$

fundamental equation, expresses $\mathcal{Q}$ 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 $S(E, V, N, \dots)$

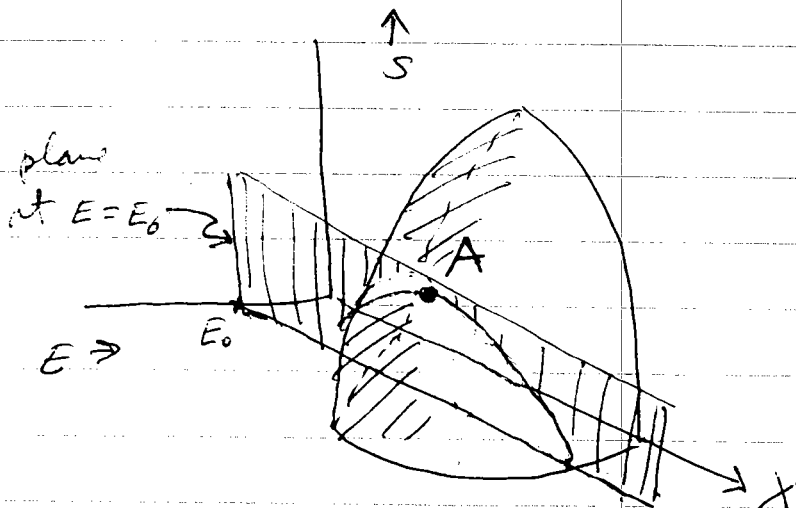
We saw that entropy is a ~~convex~~ ^{concave} function of its variables



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.

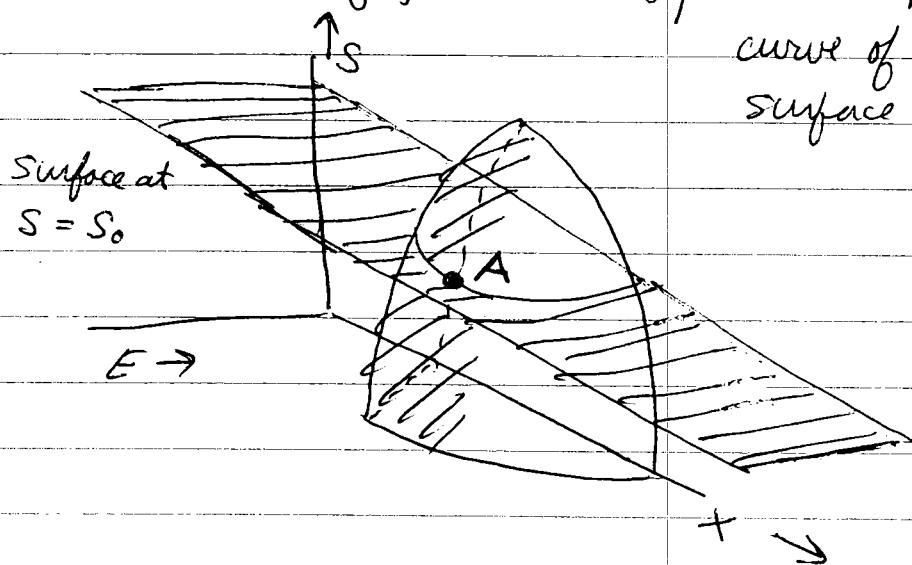
$$S_0 = \max_X [S(E_0, X)]$$



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 equilb, $d^2S < 0$. 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 equilb $d^2E > 0$
 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.

start do mechanical work add heat
 $E_0, S_0 \xrightarrow{\quad} E_1, S_0 \xrightarrow{\quad} E_0, S_1$
where $E_1 < E_0$ 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.