

Thermodynamics - Callen Chpt 1 and 2

- system with 10^{23} degrees of freedom
- we are not interested in the microscopic details, but only in average macroscopic properties
- assume that there exists a set of macroscopic variables, in terms of which the macroscopic behavior is completely described

for example: for a gas of particles one has

E	total ^{internal} energy	} <u>extensive variables</u> - grow proportional to size of system
V	volume	
N	total number of particles	

for another system there might be additional variables

ex: ferromagnets: $E, V, N, \vec{M}$ total magnetization

ferroelectrics: $E, V, N, \vec{P}$ total polarization

The first step is always to identify the relevant macroscopic variables.

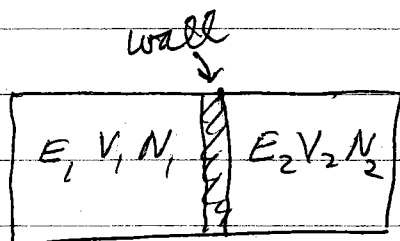
Thermodynamics can be reduced to a set of postulates, from which all other results can be derived. (just like Newton's laws determine the results for classical mechanics)

Postulate I

there exist equilibrium states characterized completely by E, V, N

criteria for equilibrium: time independent
does not depend on history

we are interested here only in equilibrium states



Basic question of thermodynamics

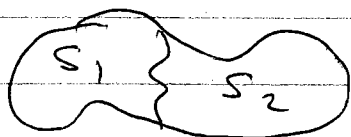
two systems in equilibrium,
separated by a wall (a constraint,
what happens if the wall is
removed (constraint relaxed) ?

Postulate II

There exists a function of the extensive
macroscopic variables, called the entropy S .
the value of S is maximized when a constraint
is removed.

Postulate III

The entropy S is additive over subsystems.
 S is a continuous and differentiable and
increasing function of the total internal
energy E .



$$S(E, V, N)$$

$$S = S_1 + S_2$$

$$\left(\frac{\partial S}{\partial E}\right)_{V, N} > 0$$

monotonic
increasing
in E

Note: additivity of subsystems is only valid when one has short range interactions, so that

$$E = E_1 + E_2$$

more generally, $E = E_1 + E_2 + E_{12}$ ← interaction energy between subsystem 1 and 2

E_1	E_2
V_1	V_2

but $E_1 \sim V_1$, $E_2 \sim V_2$

if interaction is short range then

$E_{12} \sim A$ area of wall separating subsystems

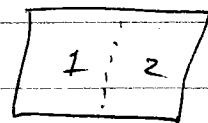
as $V \rightarrow \infty$, $\frac{A}{V} \rightarrow 0$, so energy is additive

when this assumption of additivity fails, the limit $V \rightarrow \infty$ [called the thermodynamic limit] may depend on the shape of the system.

$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

If we view the subsystems as only conceptually the two halves of a single system (rather than physically distinct subsystems) then

$$S(E, V, N) = 2 S(E/2, V/2, N/2)$$



or more generally

($\lambda = 1/2$ in above ex)

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

entropy is homogeneous 1st order function of the extensive var

$$S(E, V, N) = N S\left(\frac{E}{N}, \frac{V}{N}, 1\right) \equiv N s(u, v)$$

where

$$u = \frac{E}{N} \quad \text{energy per particle}$$

$$v = \frac{V}{N} \quad \text{volume per particle}$$

$$s = \frac{S}{N} \quad \text{entropy per particle}$$

S, E, N, V are extensive - grow prop to volume
 s, u, v are intensive - become constant as $N \rightarrow \infty$
 take thermodynamic limit

S is monotonic increasing function of E
 $\Rightarrow$ we can invert the function to get

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

Postulate IV

States for which $\left(\frac{\partial E}{\partial S}\right)_{N, V} = 0$

(this will turn out to correspond to $T=0$) $\uparrow$ constant N and V

have $S=0$ zero entropy

(Planck's extension of Nernst's 3rd law of thermo)

Conditions for equilibrium

$$E(S, V, N)$$

Define: $\left(\frac{\partial E}{\partial S}\right)_{V, N} = T$ temperature

$$-\left(\frac{\partial E}{\partial V}\right)_{S, N} = p \text{ pressure}$$

$$\left(\frac{\partial E}{\partial N}\right)_{V, S} = \mu \text{ chemical potential}$$

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

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

T, p, μ are intensive parameters since they are derivatives with respect to extensive parameters

When $dN = 0$, $dE = \underbrace{TdS} - \underbrace{pdV}$

$\nearrow$ mechanical work done by system
 $= dQ$ heat absorbed by system

heat absorbed $\Rightarrow$ entropy increases

Alternatively, thinking of entropy (not energy) as the basic thermo function

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

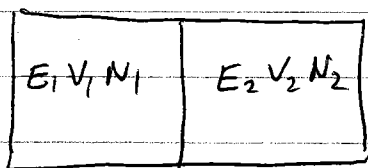
$$T dS = dE + p dV - \mu dN$$

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

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

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

Thermal equilibrium



$$E = E_1 + E_2$$

$$S = S_1(E_1, N_1, V_1) + S_2(E_2, N_2, V_2)$$

↑ moveable, impermeable, insulating wall.

as long as wall is in place, subsystems cannot exchange energy, volume, or particles.

- 1) suppose now the wall is changed to a thermally conducting one, so the systems can exchange energy? what will be the new E_1 and E_2 after the system equilibrates?

$E = E_1 + E_2$ is fixed constant by conservation of energy

But E_1 and $E_2 = E - E_1$ can change

$$E = E_1 + E_2 \quad \text{fixed} \rightarrow dE = dE_1 + dE_2 = 0$$

$$dE_2 = -dE_1$$

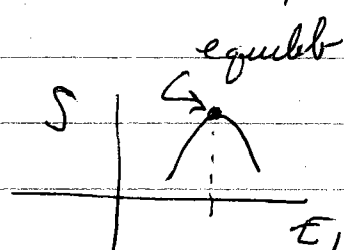
change in entropy
as system equilibrates

$$S = S_1 + S_2$$

$$dS = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2$$

$$= \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1$$



equilibrium is when S becomes maximum

$\rightarrow dS = 0$, i.e. S will not change for small changes in dE_1

$$\Rightarrow \boxed{T_1 = T_2}$$

system is in equilibrium when the two subsystems have the same temperature.

Mechanical Equilibrium

$\Rightarrow$ Now suppose the wall is made thermally conducting
AND it is allowed to slide.

$$E = E_1 + E_2$$

$$V = V_1 + V_2$$

V_1 and $V_2 = V - V_1$ may change, but total volume V stays fixed

$$\Rightarrow dE_1 = -dE_2$$

$$dV_1 = -dV_2$$

as system equilibrates the change in entropy is

$$\begin{aligned}
 dS &= \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} dV_1 + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} dV_2 \\
 &= \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{P_2}{T_2} dV_2 \\
 &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_2
 \end{aligned}$$

$$\begin{aligned}
 dS = 0 \quad \text{at equilib} \quad \text{so} \quad &\rightarrow T_1 = T_2 \\
 &P_1 = P_2
 \end{aligned}$$

when volume can change, equilib is reached when pressure of ~~subsystem~~ subsystems are equal.

Chemical Equilibrium

3) Now suppose wall becomes conducting, can slide, and is permeable to particles?

$$E = E_1 + E_2 \quad \Rightarrow \quad dE_1 = -dE_2$$

$$V = V_1 + V_2 \quad \Rightarrow \quad dV_1 = -dV_2$$

$$N = N_1 + N_2 \quad \Rightarrow \quad dN_1 = -dN_2$$

tot number N fixed, but N_1 and $N_2 = N - N_1$ vary

$$\begin{aligned}
 dS &= \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} dN_1 \\
 &\quad + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} dN_2
 \end{aligned}$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1$$

$$dS = 0 \Rightarrow T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2$$

when particles can be exchanged, equilib is reached when the subsystems have equal chemical potential.

The role of statistical mechanics is to calculate the entropy from the microscopic details of the system. Once the entropy is known, all thermodynamic properties follow.

Convexity of the Entropy

From postulate II we know S will be maximized whenever a constraint is removed. We can use this to show that S is a convex function of its variables. Consider a system that we conceptually split in half (no physical wall)

$\frac{E}{2} + \Delta E$	$\frac{E}{2} - \Delta E$
$\frac{N}{2}$	$\frac{N}{2}$
$\frac{V}{2}$	$\frac{V}{2}$

in equilibrium, $\Delta E = 0$, as the two halves must have equal energy. But consider how the entropy changes if ΔE is allowed to vary.