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

V volume

N total number of particles

} __extensive__ variables
— grow proportional to size of system

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

wall

$E_1 V_1 N_1$ | $E_2 V_2 N_2$
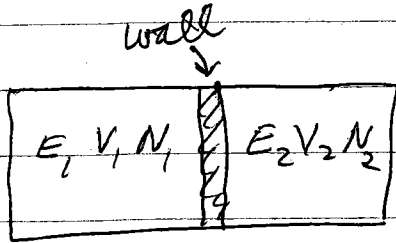
### Basic question of thermodynamics

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.
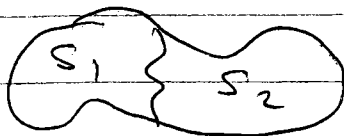
S_1 S_2

$$S = S_1 + S_2$$

$S(E, V, N)$

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

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

but $E_1 \sim V_1$, $E_2 \sim V_2$
if interaction is short range then
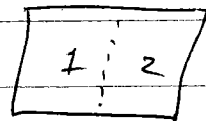$E_{12} \sim A$ area of wall separating subsystems

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

when this assumption of additivity fails, the limit $V \to \infty$ [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 halfs 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 $(\lambda = \frac{1}{2}$ 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

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

where $u = \dfrac{E}{N}$ energy per particle

        $v = \dfrac{N}{N}$ volume per particle

        $s = \dfrac{S}{N}$ entropy per particle

S, E, N, V are <u>extensive</u> — grow prop to volume

s, u, v are <u>intensive</u> — become constant as,
                     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 $\left(\dfrac{\partial E}{\partial S}\right)_{N, V} = 0$

     (this will turn out to   ↑ constant N and V

     correspond to $T=0$)

     have $S = 0$ zero entropy

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

Conditions for equilibrium
$$E(S, V, N)$$

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

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

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

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

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

T, p, μ are <u>intensive</u> parameters since they are derivatives with respect to <u>extensive</u> parameters

When $dN = 0$, $\quad dE = TdS - pdV$

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

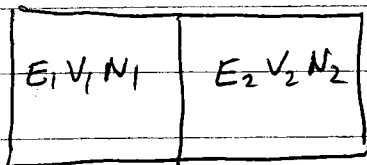$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

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

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

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

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

Thermal equilibrium

$$E = E_1 + E_2$$

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

↖ imoveable, impermiable, 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 consew of energy

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

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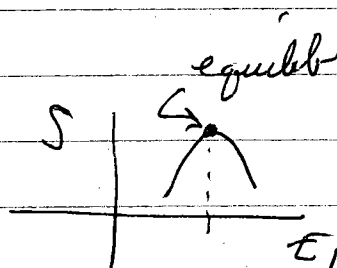$$dE_2 = -dE_1$$

change in entropy $S = S_1 + S_2$
as system equilibrates

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

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

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

equilibrium is when S becomes <u>maximum</u>

$$\Rightarrow \quad dS = 0 \quad , \text{ ie} \quad S \text{ will not change for small}$$
changes in dE_1

$$\Rightarrow \quad \boxed{T_1 = T_2} \qquad \text{system is in equilibrium when the}$$
two subsystems have the same
temperature.

<u>Mechanical Equilibrium</u>

2) Now suppose the wall is made thermally conducting
  <u>AND</u> it is allowed to slide.

$$E = E_1 + E_2$$
$$V = V_1 + V_2 \qquad \qquad V_1 \text{ and } V_2 = V - V_1 \text{ may change, but}$$
$$\text{total volume } V \text{ stays fixed}$$

$$\Rightarrow dE_1 = -dE_2$$
$$dV_1 = -dV_2$$

as system equilibrates the change in entropy is

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1 N_1} dV_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2 N_2} dV_2$$

$$= \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{P_2}{T_2} dV_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_2$$

$dS = 0$ at equilib so $\Rightarrow$ $T_1 = T_2$
$$P_1 = P_2$$

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

Chemical Equilibrium

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

$$E = E_1 + E_2 \Rightarrow dE_1 = -dE_2$$
$$V = V_1 + V_2 \Rightarrow dV_1 = -dV_2$$
$$N = N_1 + N_2 \Rightarrow dN_1 = -dN_2$$

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

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1 N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1 V_1} dN_1$$

$$+ \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2 N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2 V_2} dN_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1$$

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

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 posulate 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

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

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