Thermodynamics — Callen Chpt 1 + 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

$$E \qquad \text{total } \overset{\text{internal}}{\text{energy}}$$
$$V \qquad \text{volume}$$
$$N \qquad \text{total number of particles}$$

$\left.\begin{array}{c} \\ \\ \end{array}\right\}$ 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

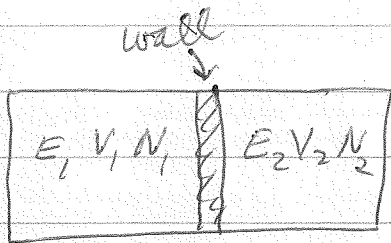The first step is always to identify the relevant macroscopic variables.

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

$$\boxed{E_1 V_1 N_1 \quad\Big|\quad E_2 V_2 N_2}$$

Basic question of thermodynamics

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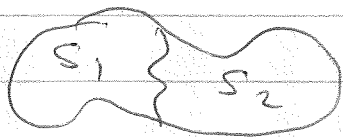
Postulate II

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.

$$S = S_1 + S_2$$

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

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} > 0 \qquad \text{monotonic increasing in } E$$

(alternatively, additivity of entropy is only strictly valid in the limit of large system sizes)

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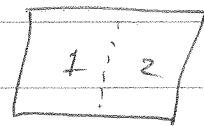$E_{12} \sim A$ area of wall separating subsystems

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 halves of a single system (rather than physically distinct subsystems) then

$$S(E, V, N) = 2S(E/2, V/2, N/2)$$
or $S(\frac{E}{2}, \frac{V}{2}, \frac{N}{2}) = \frac{1}{2}S(E, V, N)$
or more generally   ($\lambda = \frac{1}{2}$ in above ex)

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

$\Rightarrow$ In thermodynamic limit, the entropy is homogeneous 1st order function of the extensive vars

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

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

where $\quad u = \frac{E}{N}$ energy per particle $\qquad s(u,v) = S\left(\frac{E}{N}, \frac{V}{N}, 1\right)$

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

$\qquad s = \frac{S}{N}$ 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,
$\qquad\qquad\qquad\qquad$ take thermodynamic limit

S is monotonic increasing function of E

$\Rightarrow$ we can invert the function to get

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

<u>Postulate IV</u>

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

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

$\qquad$ have $S = 0$ $\qquad$ zero entropy

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

Conditions for Equilibrium

Considering $E(S,V,N)$ as the basic thermodynamic function, we can define (ie name) its partial derivatives as:

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} \equiv T \qquad \text{temperature}$$

subscripts mean derivative is taken keeping these variables held constant

$$-\left(\frac{\partial E}{\partial V}\right)_{S,N} \equiv p \qquad \text{pressure}$$
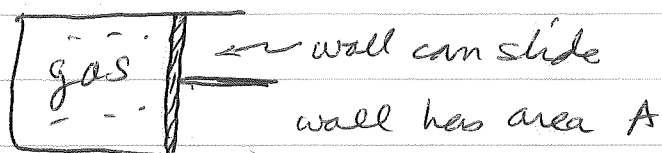
$$\left(\frac{\partial E}{\partial N}\right)_{S,V} \equiv \mu \qquad \text{chemical potential}$$

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

$$\Rightarrow \boxed{dE = T\,dS - p\,dV + \mu\,dN}$$

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

The definition of pressure above agrees with the mechanical notion that pressure is force per unit area. Consider a gas confined in the chamber of a piston.

gas ← wall can slide

wall has area A

If the chamber is thermally insulating so no heat is added or taken out, and the gas is allowed to expand by moving the piston wall a distance Δx, then the work done by the gas on the wall is $F^{total} \Delta x = p A \Delta x = p \Delta V$ where $\Delta V = A \Delta x$ is the change in volume. Since the gas is not heated (chamber thermally insulating) and it does mechanical work, the energy of the gas must decrease by the work done

$$\Rightarrow \quad \Delta E = -p \Delta V$$

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

↑
constant S means no heat is exchanged with gas and outside world.

when $dN = 0$, as is the case for a gas confined to a box,

$$dE = TdS - pdV$$

Since we just showed that pdV is the mechanical work done by the gas, then $TdS = dQ$ is the heat absorbed by the gas

(change in energy) = (heat absorbed) − (mechanical work done)

heat absorbed ⟹ entropy increases
$\underline{(dQ > 0)}$ ⟹ $\underline{(TdS) > 0}$ ⟹ $\underline{dS > 0}$

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

we have

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

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

from which we have

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

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

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