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 - grows 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.

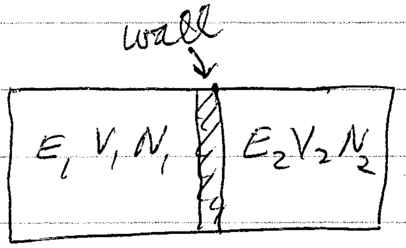
Thermodynamics can be reduced to a set of postulates, from which all other results can be derived. (just like Newton's laws determine the results for classical mechanics)

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



Basic question of thermodynamics

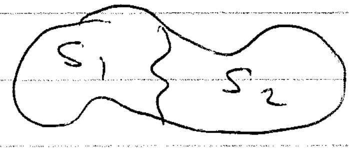
two systems in equilibrium, separated by a wall (a constraint). What happens if the wall is removed (constraint relaxed)?

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.



$S = S_1 + S_2$

$S(E, V, N)$

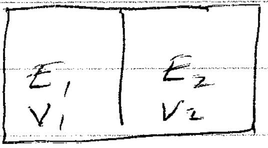
$(\partial S/\partial E)_{V,N} > 0$ monotonic increasing in E

(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

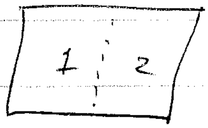
$E_{12} \sim A$ area of wall separating subsystems

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 halfs of a single system (rather than physically distinct sub-systems) then



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

or more generally ($\lambda = ½$ in above ex)

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

⇒ In thermodynamic limit, the entropy is homogeneous 1st order function of the extensive vars or $$S(E,V,N) = N\,S\left(\frac{E}{N}, \frac{V}{N}, 1\right) \equiv N\,s(u, v)$$

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

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

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

S is monotonic increasing function of E

⇒ we can invert the function to get

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

<u>Postulate IV</u>

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

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

have $S=0$ zero entropy

(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 (i.e. name) its partial derivatives as:

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

subscripts mean derivative is taken keeping these variables held constant

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

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

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

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

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