

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> - grows 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} \vec{M} total magnetization

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

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

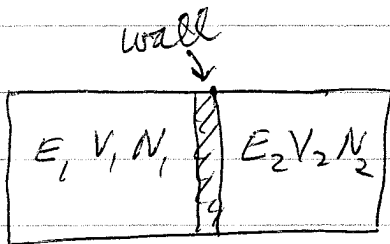
Thermodynamics can be reduced to a set of postulates, from which all other results can be derived. (just like Newton's laws determine the results for classical mechanics)

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

(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

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

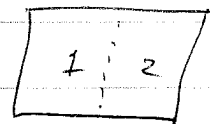
$E_{12} \sim A$ area of wall separating subsystems

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)

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

⇒ In thermodynamic limit, the entropy is homogeneous 1st order function of the extensive vars

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

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

S, E, N, V are extensive - grow prop to volume
 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

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

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

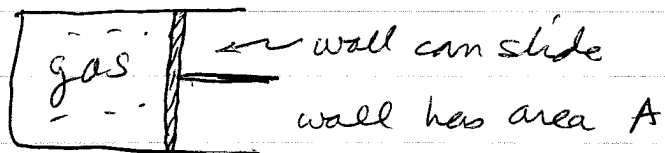
$$\left(\frac{\partial E}{\partial N}\right)_{S, V} \equiv \mu \quad \text{chemical potential}$$

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

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

T, p, μ are intensive 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.



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 $F^{\text{total}} \Delta x = p A \Delta x = p \Delta V$ 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

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

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

↑
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,

$$dE = T dS - p dV$$

Since we just showed that $p dV$ is the mechanical work done by the gas, then $T dS = dQ$ is the heat absorbed by the gas

heat absorbed \Rightarrow entropy increases

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

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

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

from which we have

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

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

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