

# 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 <sup>internal</sup> energy	} <u>extensive variables</u> - grows proportionally 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.

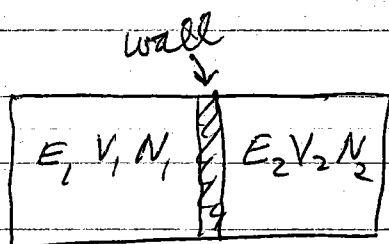
Thermodynamics can be reduced to a set of postulates, from which all other results can be derived. (just like Newton's laws determine the results for classical mechanics)

## 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

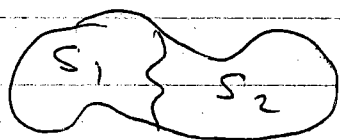
two systems in equilibrium,  
separated by a wall (a constraint,  
what happens if the wall is  
removed (constraint relaxed)?

## 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  $E$

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

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

1	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 1<sup>st</sup> order function of the extensive vars

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

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

$S, E, N, V$  are 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

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

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

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

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

$T, p, \mu$  are intensive parameters since they are derivatives with respect to extensive parameters

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

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

heat absorbed  $\Rightarrow$  entropy increases