

## 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> - grow proportional to size of system
$V$	volume	
$N$	total number of particles	

for another system there might be additional variables

ex: ferromagnets:  $E, V, N, \vec{M}$  total magnetization

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

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

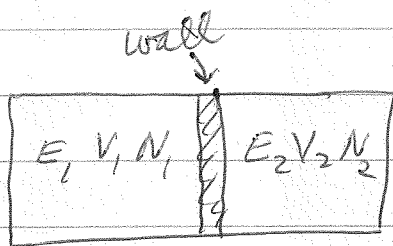
Thermodynamics can be reduced to a set of postulates, from which all other results can be derived. (just like Newton's laws determine the results for classical mechanics)

### 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

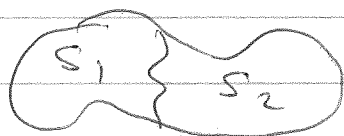
two systems in equilibrium,  
separated by a wall (a constraint)  
what happens if the wall is  
removed (constraint relaxed)?

### 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  $E$ .



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

$$S = S_1 + S_2$$

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

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

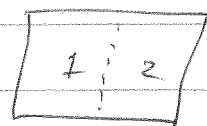
as  $V \rightarrow \infty$ ,  $\frac{A}{V} \rightarrow 0$ , so energy is additive

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

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



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

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

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  $N$  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 3<sup>rd</sup> 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

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

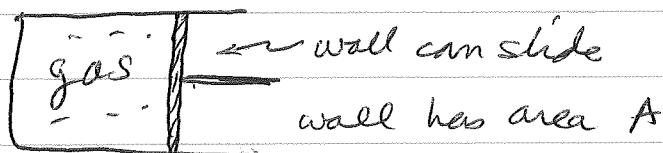
$$\left(\frac{\partial E}{\partial N}\right)_{S, V} \equiv \mu \quad \text{chemical potential}$$

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

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

$T, p, \mu$  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  $\Delta x$ , 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) as 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,

$$dE = TdS - pdV$$

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

$$\text{(change in energy)} = \text{(heat absorbed)} - \text{(mechanical work done)}$$

heat absorbed  $\Rightarrow$  entropy increases

$$\text{(dQ > 0)} \Rightarrow (TdS) > 0 \Rightarrow dS > 0$$

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

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

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

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