

### 3. Statistical Thermodynamics

#### I. Statistical formulation of a system

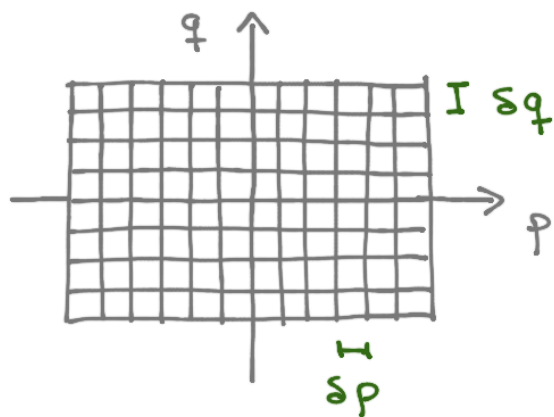
We are interested in a system that can be either a classical or a quantum system.

\* Classical system: It is described by a set of generalised coordinates  $q_1, q_2, \dots, q_f$  and conjugate momenta  $p_1, p_2, \dots, p_f$ . Once the system is specified at a given time then it is specified at any other time by virtue of the Hamilton's equations

$$\frac{dp_i}{dt} = - \frac{\partial \mathcal{H}}{\partial q_i}, \quad \frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}$$

where  $\mathcal{H}(p, q, t)$  is the Hamiltonian.

• Phase space: It is the  $(p, q)$ -space in which the system evolves with time. For computational purposes the phase space can be discretised (all cells with same size)



with  $\Delta p \Delta q = h_0$    
  $\underbrace{\hspace{2cm}}_{\text{cell area}}$    
  $\left. \begin{array}{l} \text{Classical: any} \\ \text{value} \\ \text{Quantum:} \\ \hbar = h/2\pi \end{array} \right\}$    
 (angul. momentum units)

• **Classical microstate** : Ordering and labeling each cell with an index  $r = 1, 2, \dots$ , each cell defines a **microstate** where the system can be located.

\* **Quantum system** : It is described by a wave function  $\psi(q, t)$  that depends on a set of coordinates  $q_1, q_2, \dots, q_f$ . Once the system is specified at a given time then it is specified at any other time by virtue of the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi\rangle = \hat{H} |\psi\rangle \quad (\text{general case})$$

$$\hat{H} |\psi\rangle = E_r |\psi\rangle \quad (\text{time-indep case})$$

with  $\hat{H}(p, q, t)$  being the Hamiltonian.

Each solution of the Schrödinger equation specifies a quantum state of the system.

• **Quantum microstate** : Ordering and labelling each quantum state with an index  $r = 1, 2, \dots$ , each one defines a **microstate**.

Irrespective of whether the system is classical or quantum we will never consider one unique system but a **statistical ensemble**.

Different copies of the system in the ensemble can be in different microstates and therefore can have associated different macroscopic observables (energy, magnetic moment, etc)

Ex: Three fixed particles with spin  $s = 1/2$  in presence of an external magnetic field  $H$ .  $\rightarrow + \equiv \text{up}, - \equiv \text{down}$

Microstate index $r$	Quantum numbers $m_1, m_2, m_3$	$M_r = \sum_i m_i \mu$ Total magnetic moment $M_r$	$E_r = -M_r H$ Total energy $E_r$
1	+ + +	$3\mu$	$-3\mu H$
2	- + +	$\mu$	$-\mu H$
3	+ - +	$\mu$	$-\mu H$
4	+ + -	$\mu$	$-\mu H$
5	- - +	$-\mu$	$\mu H$
6	- + -	$-\mu$	$\mu H$
7	+ - -	$-\mu$	$\mu H$
8	- - -	$-3\mu$	$3\mu H$

Microstates
Macrostate observables

Sometimes the macroscopic system is known to have some specific value of some macroscopic parameter. Then only the microstates compatible with that restriction are accessible in the ensemble.

Ex: If  $E = -\mu H \Rightarrow$  Microstates:  $(+ + -), (+ - +), (- + +)$

\* Postulate of equal a priori probabilities: An isolated system in equilibrium is equally likely to be in any of its accessible microstates compatible with  $E$  and  $X_\alpha$ .  
macrostate

\* H-theorem: If an isolated system is not equally likely to be found in any of its accessible microstates, it will evolve in time until it becomes uniformly distributed over all its accessible states

$$H \equiv \overline{\ln p_r} = \sum_r p_r \ln p_r \Rightarrow H\text{-function (negative def)}$$

probability of  $|r\rangle$

It can be proven that  $\frac{dH}{dt} \leq 0$  so that  $H$  decreases with time. Moreover

$$\frac{dH}{dt} = \sum_r \frac{dp_r}{dt} \ln p_r = 0 \text{ only if } p_r = C \text{ for all accessible microstates}$$

cte independent of  $|r\rangle$

\* Density of states and probability calculations: Consider an isolated system in equilibrium for which the total energy is known to have a constant value in some range

$$E \quad \text{and} \quad E + \delta E$$

let us introduce the fundamental quantity

$$\Omega(E) \equiv \text{Number of microstates with energy between } E \text{ and } E + \delta E$$

$$= \underbrace{\omega(E)}_{\text{"density of states"}} \delta E$$



NOTE:  $\Omega(E) = \underbrace{\Omega(0)}_0 + \omega(E) \delta E + O[(\delta E)^2] \Rightarrow$  Taylor expansion  
0 when  $\delta E = 0$

Using  $\Omega(E)$  we can write the probability  $P(y_k)$  for some other macroscopic parameter  $y$  of the system to take the value  $y_k$  as

$$P(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)}$$

$\hookrightarrow k = \text{label}$  # virtual copies in the ensemble with  $y = y_k$

so that the mean value of  $y$  is

$$\bar{y} = \frac{\sum_k \Omega(E; y_k) y_k}{\Omega(E)} = \sum_k P(y_k) y_k$$

Ex: Three fixed  $s = 1/2$  particles with  $E = -\mu H$

$(+ + -)$ ,  $(+ - +)$ ,  $(- + +)$

What is the mean magnetic moment  $\mu$  of the first spin?

$$\mu_1 = +\mu, -\mu \Rightarrow \bar{\mu}_1 = \frac{2 \times (+\mu) + 1 \times (-\mu)}{3} = \frac{1}{3} \mu$$

## II. Thermal vs Mechanical interaction

We move to describe the concepts of heat and work from a microscopic perspective. To this end we first introduce the idea of **external parameter**

\* **External parameters**: Macroscopically measurable and independent parameters  $x_1, \dots, x_n$  which are known to affect the equations of motion as they appear in the Hamiltonian.

Ex 1: Electric or magnetic external fields.

Ex 2:  $L_x, L_y, L_z$  of a box ( $V \equiv$  volume)  $\Rightarrow$  They normally appear in quantum mechanics as infinite barriers in the potential  $V(x, y, z)$ .

\* **Energy of a quantum state or microstate**: The energy levels  $E_r$  of a quantum system specify the various microstates of the system. They are obtained upon solving the Schrödinger equation with Hamiltonian  $\hat{H}(p, q; x_n)$  and read

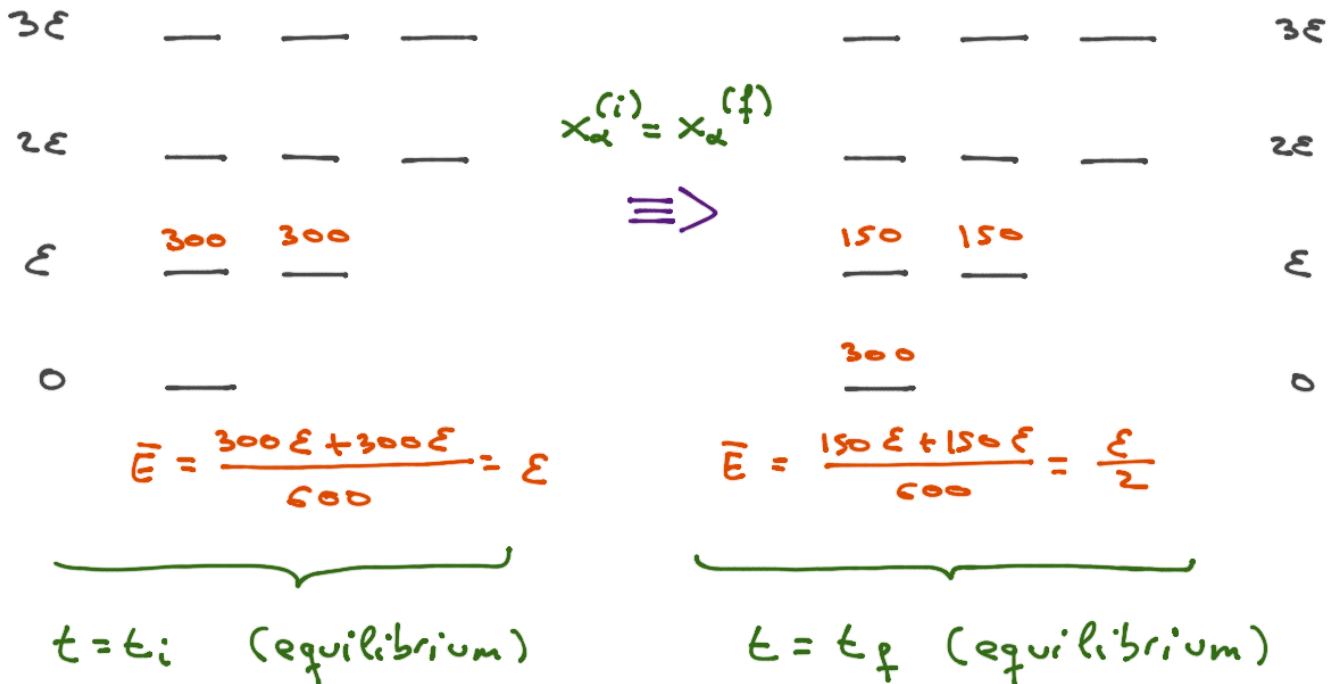
$$E_r = E_r(x_1, x_2, \dots, x_n)$$

\* **Macrostate**: A macrostate of the system is defined by specifying the external parameters  $x_n$ .

Key observation: Given a macrostate, the system can be in any one of a very large number of possible microstates!!

\* **Microscopic origin of purely thermal interaction**: Under thermal interaction the external parameters  $x_n \neq x_n(t)$  do not vary so the set of possible microstate accessible by the system does not change. The occupation numbers of the microstates just get reshuffled

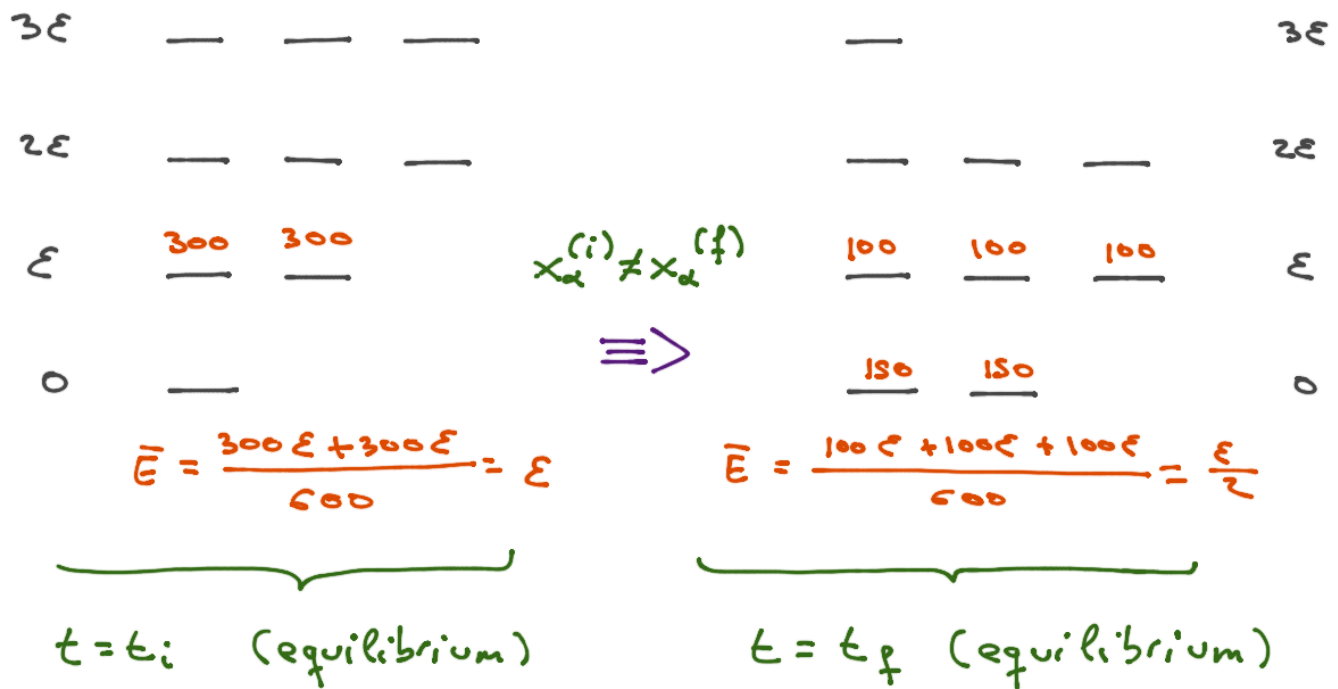
Ex: Consider an ensemble with 600 copies of the system



note: At  $t = t_i$  and  $t = t_f$  the system is in equilibrium as microstates with same  $E_r$  are equally populated.

\* Microscopic origin of purely mechanical interaction: Under mechanical interaction the external parameters  $x_n = x_n(t)$  change and so does the set of possible microstates accessible by the system.

Ex: Consider an ensemble with 600 copies of the system

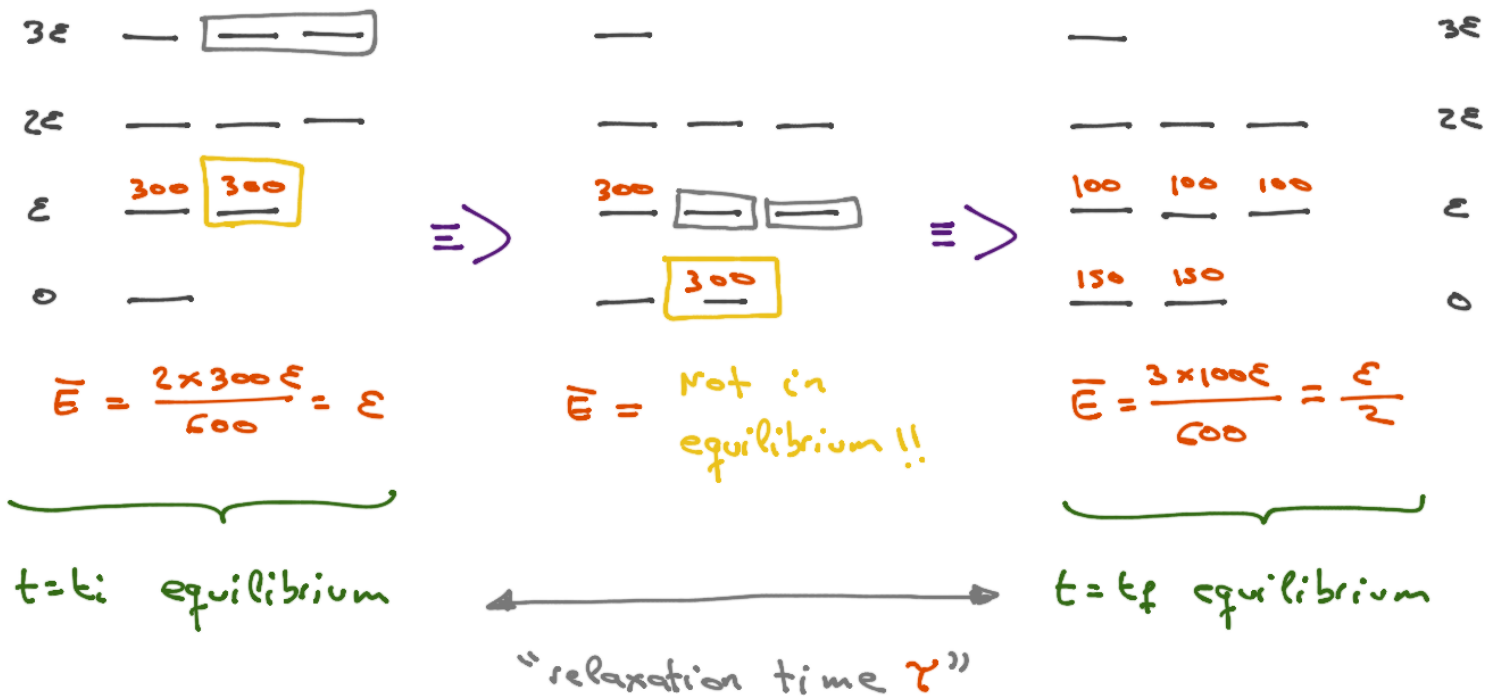


note: At  $t = t_i$  and  $t = t_f$  the system is in equilibrium as microstates with same  $E_r$  are equally populated.

\* Microscopic meaning of quasi-static: A process is said to be quasi-static when it is carried out so slowly that the system remains arbitrarily close to equilibrium at any stage.

Remark: When an energy level  $E_i(x_n)$  moves due to the change of external parameters it brings all its microstates along. Then the virtual copies are redistributed amongst levels with the same energy in order to reach equilibrium.

Ex: Consider an ensemble with 600 copies of the system



Remark: The interplay between thermal and mechanical is the origin of the word thermodynamics.

- The postulate of equal a priori probabilities and H-theorem (for isolated systems not in equilibrium) set the basis for statistical thermodynamics or equilibrium statistical mechanics.



III. Thermal interaction between macroscopic systems  
 let us consider two macroscopic systems  $A$  and  $A'$   
 in thermal interaction.



↳ Allows for a transfer of heat

We denote the **full isolated system**  $A^{(0)} = A + A'$  which  
 is described by a Hamiltonian

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_{A'} + \underbrace{\mathcal{H}^{(int)}}_{\text{interaction}}$$

- $\neq 0$  in order to trigger interactions
- very weak so  $E^{(0)} = E + E'$   
 ↳ additives

so one has that

$$E^{(0)} = E + E' = \text{constant}$$

Let us define the following quantities :

- \*  $\Omega(E) = \#$  microstates of  $A$  with energy between  $E$  and  $E + \delta E$
- \*  $\Omega'(E') = \#$  microstates of  $A'$  with energy between  $E'$  and  $E' + \delta E'$

\* Equilibrium between thermally interacting systems :

Due to energy conservation  $E^{(0)} = E + E'$ , the probability  $P(E)$  of the full system  $A^{(0)}$  to be in a configuration where  $A$  has energy between  $E$  and  $E + \delta E$

Direct product of probabilities

$$P(E) = \frac{\Omega^{(0)}(E)}{\sum_E \Omega^{(0)}(E)} = C \Omega^{(0)}(E) = C \Omega(E) \Omega'(E^{(0)} - E) \quad (1)$$

$\hookrightarrow C^{-1}$

and takes the maximum value at  $E = \tilde{E}$  when

$$\left. \frac{\partial \ln P(E)}{\partial E} \right|_{E=\tilde{E}} = \frac{1}{P} \left. \frac{\partial P(E)}{\partial E} \right|_{E=\tilde{E}} = 0$$

NOTE:  $\ln(x)$  is a monotonic function

Using (1) one has that

$$\ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E^{(0)} - E)$$

and then maximisation of  $\ln P(E)$  requires

$$\left. \frac{\partial \ln P(E)}{\partial E} \right|_{E=\tilde{E}} = \underbrace{\left. \frac{\partial \ln \Omega(E)}{\partial E} \right|_{E=\tilde{E}}}_{\beta(\tilde{E})} + \underbrace{\left. \frac{\partial \ln \Omega'(E')}{\partial E'} \right|_{E'=\tilde{E}'}}_{\beta'(\tilde{E}')} \underbrace{\left. \left( \frac{\partial E'}{\partial E} \right) \right|_{E=\tilde{E}}}_{-1} = 0$$

$$\Rightarrow \beta(\tilde{E}) = \beta'(\tilde{E}')$$

$E^{(0)} - \tilde{E}$

Important: The most likely state for the  $A^{(s)} = A + A'$  system occurs at an energy  $\tilde{E}$  where

$$\beta(\tilde{E}) = \beta' \underbrace{(\tilde{E}^{(s)} - \tilde{E})}_{\tilde{m}'}$$

with

$$\beta(E) \equiv \frac{\partial \ln \Omega}{\partial E}$$

↳  $\beta \equiv$  growth rate of # microstates with energy

Note that  $[\beta] = \text{E}^{-1}$  so it can be used to define a temperature

$$T \equiv \frac{1}{k\beta} \quad \text{with} \quad k = 1.38 \times 10^{-16} \frac{\text{erg}}{\text{deg}}$$

↳ Boltzmann

and the  $P(E)$  is maximised when

$$\beta = \beta' \Leftrightarrow T = T' \approx \text{Equilibrium}$$

Important: Defining the entropy  $S$  as

$$S \equiv k \ln \Omega$$

"Boltzmann entropy"  
[valid at equilibrium]

one has that

$$k\beta = k \frac{\ln \Omega}{\partial E} = \frac{\partial S}{\partial E} = \frac{1}{T}$$

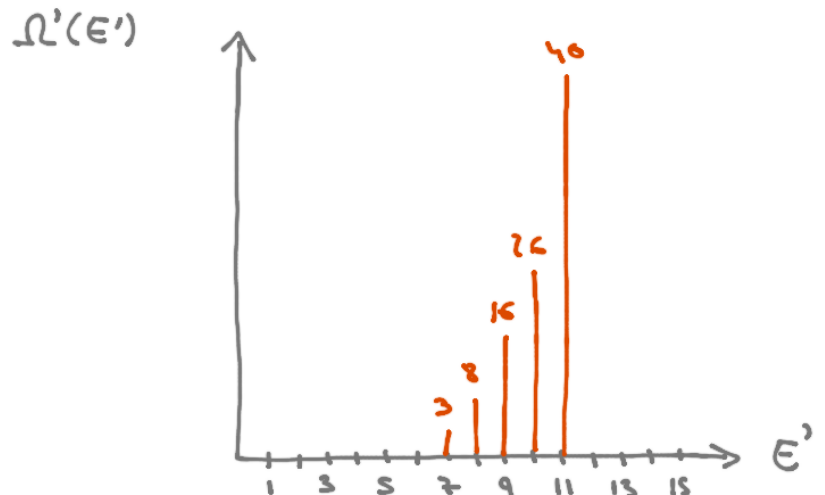
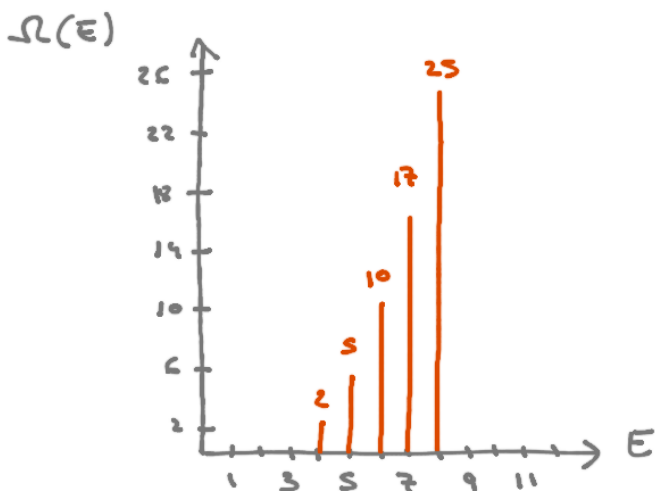
Maxwell relation  $T = \frac{\partial E}{\partial S}$

and maximisation of  $\ln P(E)$  with

$$\ln P(E) = \ln C + \underbrace{\ln \Omega}_{\frac{S}{k}} + \underbrace{\ln \Omega'}_{\frac{S'}{k}} \Rightarrow \underbrace{S + S'}_{\text{at equilibrium}} = \text{maximum}$$

Comment: Since the final probability  $P(E)$  is maximum and thus never less than the original one, the entropy never decreases.

Ex: Microstates of system A, A' and A<sup>(0)</sup>. Suppose that the energy E<sup>(0)</sup> measured experimentally is E<sup>(0)</sup> = 15.



Data in the figures corresponds with the table:  $[E^{(s)} = 15]$

$E$	$E'$	$\Omega(E)$	$\Omega(E')$	$\Omega^{(s)}(E)$
4	11	2	40	80
5	10	5	26	130
6	9	10	16	160 } Maximise
7	8	17	8	136
8	7	25	3	75

Determine  $\tilde{E}$  and  $P(\tilde{E})$ :

$$\Omega_{\text{tot}}^{(s)} = 581 = C^{-1}$$

- $\tilde{E} = 6 \Rightarrow P(\tilde{E}) = \frac{\Omega^{(s)}(\tilde{E})}{\Omega_{\text{tot}}^{(s)}} = \frac{160}{581} \approx 27\%$

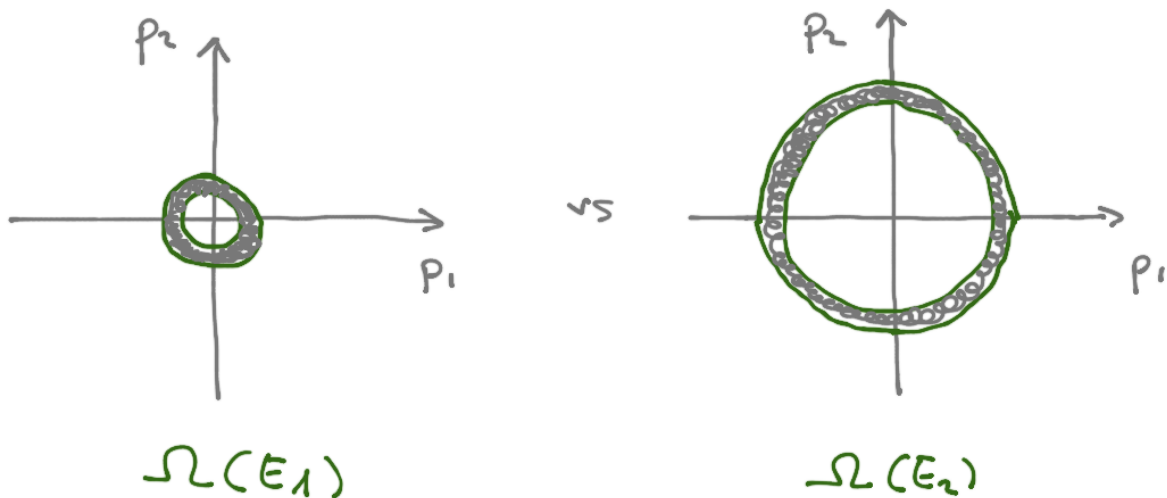
Remark on absolute temperature: The temperature  $T$  is understood microscopically as

$$\frac{1}{kT} \equiv \beta \equiv \frac{\partial \ln \Omega}{\partial E}$$

a) System described by  $\mathcal{L}^{(\text{kin})}$  for particles in  $(p, q)$ -space: Using generalised coordinates  $q_1, \dots, q_f$  and momenta  $p_1, \dots, p_f$  the phase space is

NOTE: Integration over coordinates  $\int dq_1 \dots dq_f = V$  (volume)



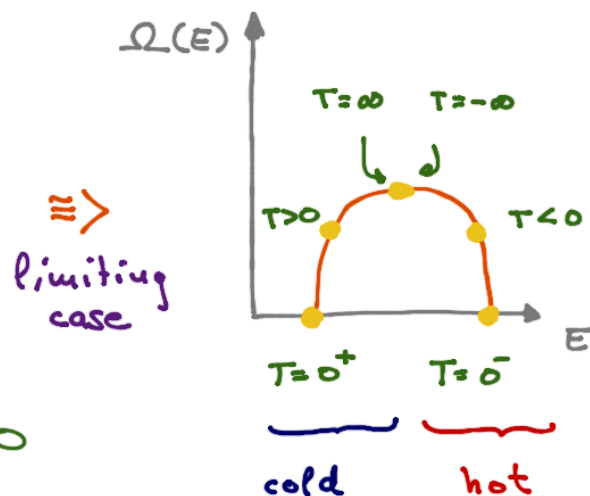
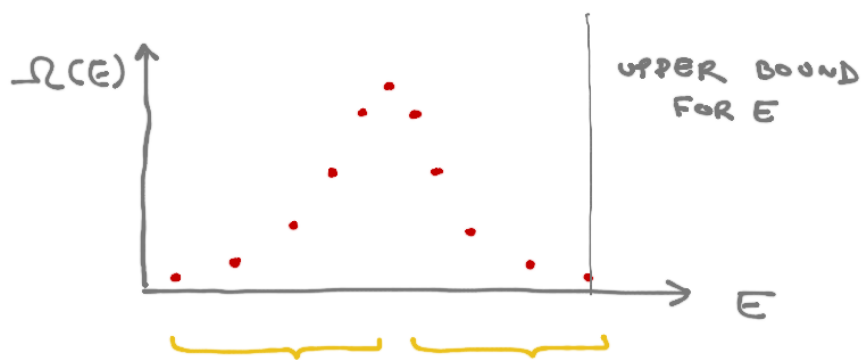


So  $\Omega(E)$  increases continuously with  $E$ . As a result

$$\frac{\partial \ln \Omega}{\partial E} \equiv \beta \equiv \frac{1}{kT} > 0 \Rightarrow T > 0$$

Systems like this are called ordinary systems and are described using translational degrees of freedom.

b) System described by spin degrees of freedom: Using  $S = \pm$  degrees of freedom we have seen before that  $\Omega(E)$  with  $E = -MH$  first increases and then decreases



$$T > 0 : \frac{\partial \ln \Omega}{\partial E} > 0 \quad \frac{\partial \ln \Omega}{\partial E} < 0 : T < 0$$

\* Heat reservoirs and 2<sup>nd</sup> law of thermodynamics:

Let's have a system  $A$  in contact with a heat reservoir  $A'$  so that

$$\frac{\bar{E}}{E'} \ll 1 \quad [\text{Heat reservoir much larger}]$$

By definition, the temperature  $\beta' = \frac{1}{kT}$  of the reservoir does not change if the small system absorbs/emits a small heat amount  $Q'$

$$\begin{aligned} \ln \Omega'(E' + Q') - \ln \Omega'(E') &= \\ &= \left( \frac{\partial \ln \Omega'}{\partial E'} \right) Q' + \frac{1}{2} \left( \frac{\partial^2 \ln \Omega'}{\partial E'^2} \right) Q'^2 + \dots \\ &= \beta' Q' + \dots \end{aligned}$$

$$\Rightarrow \ln \Omega'(E' + Q') - \ln \Omega'(E') = \beta' Q' = \frac{Q'}{kT}$$

lowest order

$$\Rightarrow k \ln \Omega'(E' + Q') - k \ln \Omega'(E') = \frac{Q'}{T}$$

$$\Rightarrow \Delta S' = \frac{Q'}{T} \quad \rightsquigarrow \quad dS = \frac{dQ}{T} \quad [2^{\text{nd}} \text{ law}]$$

infinitesimal level

\* Sharpness of  $P(E)$  : let us investigate  $P(E)$  in a vicinity of  $E = \tilde{E}$  by expanding in powers of  $\eta = E - \tilde{E}$

$$\ln \Omega(E) = \ln \Omega(\tilde{E}) + \underbrace{\frac{\partial \ln \Omega}{\partial E}}_{\beta(\tilde{E})} \Big|_{E=\tilde{E}} \eta + \frac{1}{2} \underbrace{\left( \frac{\partial^2 \ln \Omega}{\partial E^2} \right)}_{-\lambda(\tilde{E})} \Big|_{E=\tilde{E}} \eta^2 + \dots$$

$$= \ln \Omega(\tilde{E}) + \beta(\tilde{E}) \eta - \frac{1}{2} \lambda(\tilde{E}) \eta^2 + \dots \quad \Rightarrow \text{System A}$$

Let us now consider the heat reservoir with  $E' = E^{(0)} - E$  so that

$$E' - \tilde{E}' = (E^{(0)} - E) - (E^{(0)} - \tilde{E}) = -E + \tilde{E} = -\eta$$

↳ energy conservation

so

$$\ln \Omega'(E') = \ln \Omega'(\tilde{E}') + \beta'(-\eta) - \frac{1}{2} \lambda'(-\eta)^2 + \dots \quad \Rightarrow \text{System A'}$$

Combining the expansions of A and A' one finds [lowest order]

$$\ln [\underbrace{\Omega(E)}_{C^{-1} P(E)} \cdot \underbrace{\Omega'(E')}_{C^{-1} P(\tilde{E}')}] = \ln [\underbrace{\Omega(\tilde{E}) \Omega(\tilde{E}')}_{C^{-1} P(\tilde{E})}] + \underbrace{(\beta - \beta')}_{\text{equilibrium } \beta = \beta'} \eta - \frac{1}{2} \underbrace{(\lambda + \lambda')}_{\lambda_0} \eta^2$$

$$\Rightarrow P(E) = P(\tilde{E}) e^{-\frac{1}{2} \lambda_0 (E - \tilde{E})^2} \quad \approx \text{Gaussian distrib} \Rightarrow \tilde{E} = \bar{E}$$

NOTE: If  $\Omega \propto E^{\frac{\gamma}{\#f}}$   $\Rightarrow \lambda \propto - \frac{\partial^2 \ln \Omega}{\partial E^2} \Big|_{E=\tilde{E}} = -\frac{\gamma}{\#f} \left( -\frac{1}{\tilde{E}^2} \right) = \frac{\#f}{\tilde{E}^2} > 0$

#### IV. Mechanical interaction between macroscopic systems

The energy  $E_r(x_1, \dots, x_n)$  of a microstate  $r$  depends on external parameters in the Hamiltonian so that

$$dE_r = \sum_{\alpha=1}^n \frac{\partial E_r}{\partial x_\alpha} dx_\alpha .$$

When the system remains in the state  $r$  (so  $dQ = 0$ ) it performs an amount of work

$$dW_r \equiv -dE_r = \sum_{\alpha=1}^n \left( - \frac{\partial E_r}{\partial x_\alpha} \right) dx_\alpha$$

$$X_\alpha = - \frac{\partial E_r}{\partial x_\alpha} \equiv \text{Generalised force}$$

\* General density of states  $\Omega(E, x)$ : When external parameters  $x_\alpha$  change  $x_\alpha \rightarrow x_\alpha + dx_\alpha$  one has to take into account the change of the microstate energy  $E_r \rightarrow E_r + \frac{\partial E_r}{\partial x_\alpha} dx_\alpha$ .

$$Y_\alpha = \frac{\partial E_r}{\partial x_\alpha} \equiv -X_\alpha$$

For the sake of simplicity let us focus on just one external parameter  $x$ . The previous discussion then reduces to

$$\underbrace{\Omega(E, x)}_{\substack{E+\delta E \\ x=\text{fixed}}} = \sum_Y \underbrace{\Omega_Y(E, x)}_{\substack{E+\delta E \\ Y+\delta Y}} \Rightarrow \text{\# states } r \text{ with energy between } E \text{ and } E+\delta E \text{ at value } x \text{ and with } \frac{\partial E_r}{\partial x} \text{ between } Y \text{ and } Y+\delta Y$$

NOTE: The sum is over states  $r$  with all possible values of  $Y = \frac{\partial E_r}{\partial x}$ .

note: It is important to keep track of the quantity  $\gamma$  because, as long as  $x \rightarrow x + dx$ , some microstates will enter the band  $E + \delta E$  and some others will go out. For the microstate  $r$  this information is encoded in  $\gamma = \frac{\partial E_r}{\partial x}$ .

Let us denote

$$\sigma_\gamma(E) = \underbrace{\frac{\Omega_\gamma(E, x)}{\delta E}}_{\text{homogeneous density of states}} \underbrace{\gamma dx}_{\text{band width}}$$

the number of states within an energy  $\gamma dx$  below  $E$ .

Then the total number of states  $\sigma(E)$  whose energy is lifted from a value less to a value greater than  $E$  is given by

$$\sigma(E) = \sum_\gamma \frac{\Omega_\gamma(E, x)}{\delta E} \gamma dx = \frac{\Omega(E, x)}{\delta E} \bar{\gamma} dx$$

where

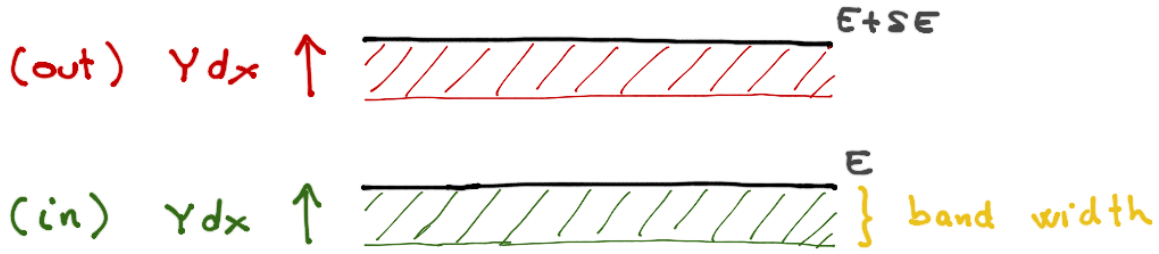
$$\bar{\gamma}(E, x) = \frac{1}{\Omega(E, x)} \sum_\gamma \Omega_\gamma(E, x) \gamma$$

so that

$$\bar{\gamma} = \overline{\frac{\partial E_r}{\partial x}} \equiv -\overline{X}$$

But this is not the end of the story as other states with energy less than  $E + \delta E$  will go out.





As a result of the above discussion one has that

$$\frac{\partial \Omega(E, x)}{\partial x} dx = +\sigma(E) - \sigma(E + \delta E) = - \frac{\partial \sigma}{\partial E} \delta E$$

Using  $\sigma(E) = \frac{\Omega(E, x)}{\delta E} \bar{\gamma} dx$  and  $\bar{\gamma} = \bar{\gamma}(E, x)$  one finds  
 $\delta E$  indep of  $E$

$$\frac{\partial \Omega(E, x)}{\partial x} = - \frac{\partial}{\partial E} (\Omega \bar{\gamma}) = - \frac{\partial \Omega}{\partial E} \bar{\gamma} - \Omega \frac{\partial \bar{\gamma}}{\partial E} \quad \left( \times \frac{1}{\Omega} \right)$$

$$\Rightarrow \frac{\partial \ln \Omega}{\partial x} = - \frac{\partial \ln \Omega}{\partial E} \bar{\gamma} - \frac{\partial \bar{\gamma}}{\partial E} \approx - \frac{\partial \ln \Omega}{\partial E} \bar{\gamma} = \beta \bar{X}$$

$\propto \frac{N}{E}$   $N \rightarrow \infty$   
(see note)

NOTE:  $\sum_{i=1}^N p_{ix}^2 + p_{iy}^2 + p_{iz}^2 = 2mE = R^2 \Rightarrow R \sim E^{1/2}$

$\Rightarrow$  Volume of states with energy less than  $E$  goes as

$$\Phi(E) \sim R^{3N} \sim E^{\frac{3}{2}N} \Rightarrow \Omega(E) = \Phi(E + \delta E) - \Phi(E)$$

$$= \frac{\partial \Phi}{\partial E} \delta E = \frac{3}{2} N E^{\frac{3}{2}N-1} \delta E$$

$$\Rightarrow \frac{\partial \ln \Omega}{\partial E} \sim \frac{N}{E}$$

$N \sim$  Avogadro's number

The microscopic interpretation of the generalised force  $\bar{X}_\alpha$  is then

$$\frac{\partial \ln \Omega}{\partial x_\alpha} = \beta \bar{X}_\alpha$$

\* Equilibrium between interacting systems

Let us consider a quasi-static process that brings system A to equilibrium with system A'. More concretely system A changes from an equilibrium state  $(\bar{E}, x_\alpha)$  to another equilibrium state  $(\bar{E} + d\bar{E}, x_\alpha + dx_\alpha)$ . One then has that

$$\begin{aligned} d \ln \Omega &= \frac{\partial \ln \Omega}{\partial \bar{E}} d\bar{E} + \sum_{\alpha=1}^n \frac{\partial \ln \Omega}{\partial x_\alpha} dx_\alpha \\ &= \beta d\bar{E} + \sum_{\alpha=1}^n \beta \bar{X}_\alpha dx_\alpha \\ &= \beta (d\bar{E} + \sum_{\alpha=1}^n \bar{X}_\alpha dx_\alpha) \equiv \beta dQ \end{aligned}$$

↳ Microscopic definition of heat.

Therefore :

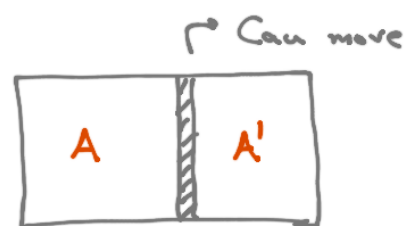
$$\begin{aligned} i) \quad dQ &\equiv d\bar{E} + \underbrace{\sum_{\alpha=1}^n \bar{X}_\alpha dx_\alpha}_{dW} = d\bar{E} + dW \Rightarrow \begin{array}{l} 1^{\text{st}} \text{ law} \\ \text{of} \\ \text{thermodynamics} \end{array} \\ dW &\equiv \sum_{\alpha=1}^n \bar{X}_\alpha dx_\alpha \Rightarrow \text{Microscopic work (definition)} \end{aligned}$$

$$ii) \quad dQ \equiv \frac{1}{\beta} d \ln \Omega = T \overbrace{\kappa d \ln \Omega}^{dS} = T dS$$

$$\Rightarrow dS = \frac{dQ}{T} \quad \equiv > \begin{array}{c} 2^{\text{nd}} \text{ law} \\ \text{of} \\ \text{thermodynamics} \end{array}$$

The set of equilibrium conditions between A and A' are easily derived starting from

$$\Omega^{(e)}(E, x_\alpha) = \Omega(E, x_\alpha) \Omega'(E', x_{\alpha'})$$



↳ allows for heat transfer

$$A : d \ln \Omega = \beta dE + \sum_{\alpha} \beta \bar{X}_{\alpha} dx_{\alpha}$$

$$A' : d \ln \Omega' = \beta' dE' + \sum_{\alpha} \beta' \bar{X}'_{\alpha} dx'_{\alpha}$$

The full  $A^{(e)} = A + A'$  is isolated  $\Rightarrow dE = -dE'$ ,  $dx_{\alpha} = -dx'_{\alpha}$   
so

$$d \ln \Omega^{(e)} = d \ln \Omega + d \ln \Omega' = (\beta - \beta') dE + \sum_{\alpha} (\beta \bar{X}_{\alpha} - \beta' \bar{X}'_{\alpha}) dx_{\alpha}$$

The equilibrium is achieved when  $\kappa \ln \Omega^{(e)} = S^{(e)} = S + S'$  is maximised

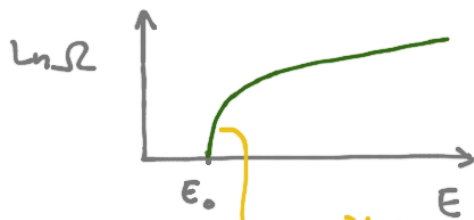
$$d \ln \Omega^{(e)} = 0 \quad \Rightarrow \quad \begin{array}{l} \beta - \beta' = 0 \\ \beta \bar{X}_{\alpha} - \beta' \bar{X}'_{\alpha} = 0 \end{array} \quad \Rightarrow \quad \begin{array}{l} \beta = \beta' \\ \bar{X}_{\alpha} = \bar{X}'_{\alpha} \end{array}$$

Same T and same gen. forces

Remark: The zeroth law then follows immediately from the equilibrium conditions.

\* The third law of thermodynamics: When  $T \rightarrow 0$  quantum systems approach the ground state  $E \rightarrow E_0$

$$\Omega(E) \sim \underbrace{(E - E_0)^{\#N}}_{\text{kinematics}} \Rightarrow$$



$$S = k \ln \Omega = k \ln(1) \rightarrow S \rightarrow 0$$

$E \rightarrow E_0$   $\hookrightarrow$  or a very small number of ground states

NOTE: In case of having  $N$  spins, then there are  $\Omega_s = 2^N$  possible spin states accessible to the system even when decreasing  $T$ . In this case

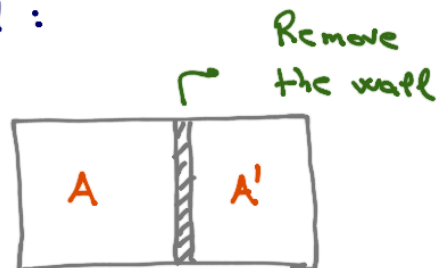
$$S \rightarrow \underline{S_0 = k \ln \Omega_s} \quad \text{as} \quad T \rightarrow 0^+$$

When kinematics is over, spin is still there !!

\* Reversibility vs irreversibility: Let us consider an isolated system  $A^{(0)} = A + A'$  where some constraints (like removing the separating wall) are relaxed. Since the system is less constrained then  $\Omega_f \geq \Omega_i$  and:

• Reversible:  $\Omega_f = \Omega_i$

• Irreversible:  $\Omega_f > \Omega_i$



## v. Microscopic description of the ideal gas

Let us consider a gas consisting of  $N$  identical molecules inside a container of volume  $V$ . The full energy of the system

$$E = \underbrace{K(\vec{p}_i)}_{\text{kinetic}} + \underbrace{U(\vec{r}_i)}_{\text{potential}} + \underbrace{E_{\text{int}}}_{\text{intramolecular interaction (for not monoatomic molecules)}}$$

with

- $K = K(\vec{p}_i) = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i^2 \Rightarrow$  Kinetic translational energy  
↳ mass of the molecule
- $U = U(\vec{r}_i) \Rightarrow$  Potential interaction between molecules
- $E_{\text{int}}(Q_1, \dots, Q_M; P_1, \dots, P_M) \Rightarrow$  Total energy due to intramolecular motion described by coordinates  $Q_1, \dots, Q_M$  and momenta  $P_1, \dots, P_M$ .

\* Ideal gas: The system is so diluted that  $U(\vec{r}_i) \sim 0$

Question: What is  $\Omega(E, V)$ ? To answer this question we have to label and count the number of cells in phase space with energy between  $E$  and  $E + \delta E$ .

↳ volume of phase space



$$\Omega(E, V) \propto \int_E^{E+\Delta E} d^3\vec{r}_1 \cdots d^3\vec{r}_N d^3\vec{p}_1 \cdots d^3\vec{p}_N dQ_1 \cdots dQ_M dP_1 \cdots dP_M$$

where  $d^3\vec{r}_i \equiv dx_i dy_i dz_i$  and  $d^3\vec{p}_i = dp_{ix} dp_{iy} dp_{iz}$ .

In the case of an ideal gas one has  $U(\vec{r}_i) = 0$  so we can perform the integration over  $\prod_{i=1}^N d\vec{r}_i$

$$\int_E^{E+\Delta E} d^3\vec{r}_i = V \Rightarrow \int_E^{E+\Delta E} \underbrace{\prod_{i=1}^N d\vec{r}_i}_{V^N} = V^N$$

We neglect the volume occupied by the molecules [see real gas]

and therefore

$$\Omega(E, V) \propto V^N \chi(E)$$

with

$$\chi(E) = \int_E^{E+\Delta E} d^3\vec{p}_1 \cdots d^3\vec{p}_N dQ_1 \cdots dQ_M dP_1 \cdots dP_M$$

Let us consider now the case where the gas is **monoatomic** so that  $E_{int} = 0$  and no intramolecular variables  $Q$ 's and  $P$ 's appear in the problem. Then

$$E = \frac{1}{2m} \sum_{i=1}^N \sum_{\alpha=1}^3 p_{i\alpha}^2 \Rightarrow \sum_{\alpha=1}^{3N} p_{\alpha}^2 = \underbrace{2mE}_{R(E) = (2mE)^{1/2}}$$

collective index "α"

The volume of states with energy less than  $E$  is

$$\Phi(E) \propto R(E)^{3N} = (2mE)^{\frac{3}{2}N}$$

This implies that the number of states with energy between  $E$  and  $E + \delta E$  is

$$\Omega(E, V) = \Phi(E + \delta E) - \Phi(E) = \frac{\partial \Phi}{\partial E} \delta E \propto E^{\frac{3}{2}N - 1}$$

In the limit of  $N \gg 1$  one finds

$$\Omega(E, V) = c V^N E^{\frac{3}{2}N}$$

↳ constant independent of  $V, E$

Remark: Since  $N \sim$  Avogadro's number,  $\Omega(E, V)$  grows very rapidly as a function of  $E$ .

Using  $\Omega = c V^N \chi(E)$  with  $\chi(E) = E^{\frac{3}{2}N}$  the equation of state of the ideal gas can be derived. Let us consider

$$\ln \Omega = N \ln V + \underbrace{\ln \chi(E)}_{\frac{3}{2}N \ln E} + \ln c$$

Then

$$\beta \equiv \left. \frac{\partial \ln \Omega}{\partial E} \right|_{E=\bar{E}} = \frac{3}{2} \frac{N}{\bar{E}} \Rightarrow \bar{E} = \frac{3}{2} N k T \Rightarrow \underbrace{\bar{E} = \bar{E}(T)}_{\text{Joule's exp !!}}$$

The equation of state for the ideal gas then follows from

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial v} = \frac{1}{\beta} N \frac{\partial \ln v}{\partial v} = N k T \cdot \frac{1}{v} \Rightarrow \underbrace{\bar{p} v = N k T}_{\text{equation of state for ideal gas!!}}$$

$\beta = \frac{1}{kT}$

Summary: "Statistical Thermodynamics"

$\Omega(E, x_\alpha) \equiv \#$  microstates with energy between  $E$  and  $E + \delta E$  at values  $x_\alpha$

- $S = k \ln \Omega$
- $\beta \equiv \frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E} \quad \approx \rightarrow E(T)$
- $\beta \overline{x_\alpha} = \frac{\partial \ln \Omega}{\partial x_\alpha} \quad \approx \rightarrow \text{Equation of state}$