

## 4. Statistical Ensembles

We will present different types of ensemble which are representative of wide classes of physical systems.

I. Isolated systems ( $E, N, V = \text{fixed}$ ): Microcanonical ensemble

Comment: It is very useful as having a system  $A$  interacting with a system  $A'$  can be viewed as an isolated system  $A + A'$ .

$$\text{Isolated system} \Rightarrow dE^{(s)} = 0 \Rightarrow E^{(s)} = \text{cte}$$

\* If the energy of a system  $A$  in state  $r$  is  $E_r$ , the probability of finding the system  $A$  in state  $r$  is

$$P_r = \begin{cases} C = \text{cte} & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases} \quad \text{"Microcanonical ensemble"}$$

This is nothing but the fundamental statistic postulate:

"In an equilibrium configuration the isolated system is equally likely to be found in any one of its accessible states with energy in the range  $E$  and  $E + \delta E$ "

The value of  $C$  can be determined by the normalisation condition  $\sum_r P_r = 1$ .

## II. System with specified $\bar{E}$ ( $N, V = \text{fixed}$ ): Canonical ensemble

Let us consider a small system  $A$  with  $N, V = \text{fixed}$  interacting with a heat reservoir  $A'$  so that its energy fluctuates but  $\bar{E}$  is fixed.

Question: Under conditions of equilibrium, what is the probability  $P_r$  of finding the system  $A$  in one particular microstate  $r$  of energy  $E_r$ ?

Assuming weak interaction between  $A$  and  $A'$  one has

$$E^{(0)} = E_r + E'$$

↳ additivity

and then, if  $A$  is in the one definite state  $r$ , the number of states accessible to the combined system  $A^{(0)}$  is

# microstates of  $A'$

$$P_r = C' \Omega'(E') = C' \Omega'(E^{(0)} - E_r)$$

when the energy of  $A'$  is in the range between  $E'$  and  $E' + \delta E'$ . The constant  $C'$  is obtained from

$$\sum_r P_r = 1 \quad (\text{normalisation condition})$$

where  $r$  runs over all states irrespective of their  $E_r$ .

Let us make use of the fact that

$$A \ll A' \Rightarrow E_r \ll E^{(0)}$$

so that

$$\ln \Omega'(E') = \ln \Omega'(E^{(0)} - E_r)$$

Taylor around  $E^{(0)}$   $\leftarrow$

$$= \ln \Omega'(E^{(0)}) + \frac{\partial \ln \Omega'}{\partial E'} \Big|_{(0)} \overbrace{(E' - E^{(0)})}^{-E_r} + \dots$$

$$= \ln \Omega'(E^{(0)}) - \frac{\partial \ln \Omega'}{\partial E'} \Big|_{(0)} E_r + \dots$$

$$\beta'(E^{(0)}) = \frac{1}{kT}$$

temperature  $T$   
of the heat  
reservoir  $A'$  !!

Lowest order  $\leftarrow$   $= \ln \Omega'(E^{(0)}) - \beta' E_r$

$$\Rightarrow \Omega'(E^{(0)} - E_r) = \underbrace{\Omega'(E^{(0)})}_{\text{Independent of system A (and therefore of } E_r)} \cdot e^{-\beta' E_r}$$

One then finds that

$$P_r = c' \Omega'(E^{(0)} - E_r) = c' \underbrace{\Omega'(E^{(0)})}_c e^{-\beta' E_r} = c \underbrace{e^{-\beta E_r}}_{\text{"Boltzmann factor"}}$$

NOTE: We replace  $\beta' \rightarrow \beta$  just meaning  $T$  at equilibrium.  
[ $\beta = \beta'$ ]

The constant  $C$  is independent of  $r$  and is determined by the normalisation condition

$$\sum_r P_r \stackrel{!}{=} 1 \Rightarrow C^{-1} = \sum_r e^{-\beta E_r}$$

so that

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

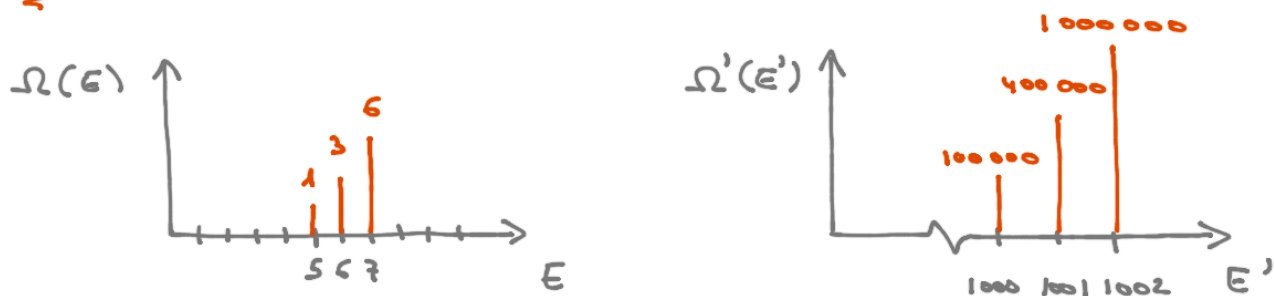
"Canonical ensemble"

Comment: Remember that  $A'$  can be in any of its large number of microstates  $\Omega'(E')$ . Note that

$$E_r \text{ increases} \Rightarrow E' \text{ decreases}$$

and, since  $\Omega'(E')$  is a very rapidly changing monotonic function of  $E'$  (ordinary system), the number of microstates accessible to the reservoir is drastically reduced. Then  $P_r$  is drastically (exponentially) suppressed.

Ex: Systems  $A$  and  $A'$  with  $E^{(0)} = 1007$ :



We have obtained the probability  $P_r$  of finding the system  $A$  in one particular microstate with energy  $E_r$ . The probability  $P(E)$  of finding  $A$  with an energy between  $E$  and  $E + \delta E$  is given by

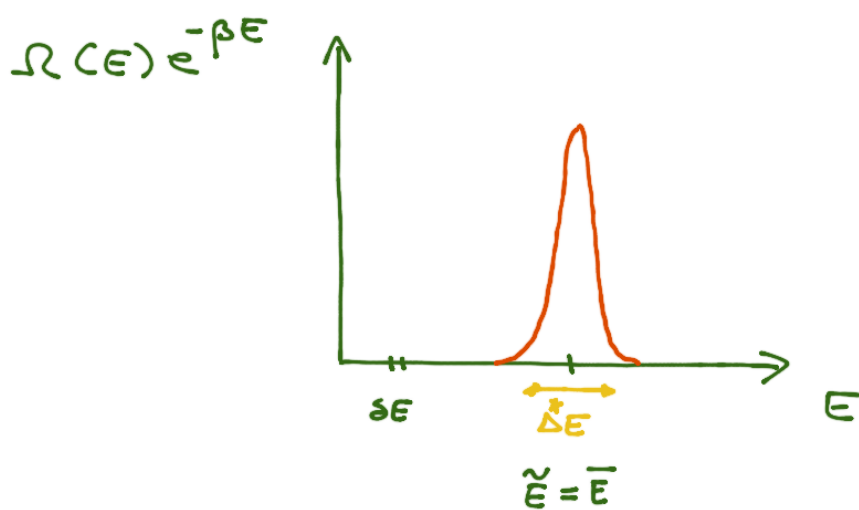
$$P(E) = \sum_r P_r \quad \text{where } r \text{ is such that } E < E_r < E + \delta E$$

equivalently

$$P(E) = C \underbrace{\Omega(E)}_{\# \text{ microstates} = \text{multiplicity}} \underbrace{e^{-\beta E}}_{\text{weight}}$$

NOTE: Due to the behaviours

- $\Omega(E) \Rightarrow$  Rapidly increasing with  $E$
- $e^{-\beta E} \Rightarrow$  Rapidly decreasing with  $E$



NOTE:  $\Delta^*E = \sqrt{(\Delta E)^2} \equiv$  root mean square deviation from  $\bar{E}$

\* Mean values : Let  $y$  be a quantity taking a value  $y_r$  at microstate  $r$ . Then

$$\bar{y} = \frac{\sum_r y_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

where  $r$  runs over all microstates of  $A$ .

Remark : The heat reservoir  $A'$  plays an auxiliary role only setting the temperature  $T$ . Nothing else depends on it.

### III. Simple applications of the canonical ensemble

1. Paramagnetism : It is a form of magnetism by which certain materials are weakly attracted by an external magnetic field  $H$  and form internal (induced) magnetic fields in the direction of the applied magnetic field.

Let us consider a substance with  $N_0$  magnetic  $\frac{\text{atoms}}{\text{volume}}$  with  $s = \frac{1}{2}$  at temperature  $T$  and intrinsic magnetic moment  $\mu$

$$\text{each atom} \begin{cases} \text{parallel } |+\rangle : E_+ = -\mu H \Rightarrow P_+ = C e^{-\beta E_+} = C e^{\frac{\mu H}{kT}} \\ \text{anti-parallel } |-\rangle : E_- = \mu H \Rightarrow P_- = C e^{-\beta E_-} = C e^{-\frac{\mu H}{kT}} \end{cases}$$

Then one has that

$$P_+ = c e^{\frac{\mu H}{kT}} \quad , \quad P_- = c e^{-\frac{\mu H}{kT}}$$

very likely                      very suppressed

Computing  $\bar{\mu}_H$  of a single atom one finds

$$\bar{\mu}_H = \frac{\mu P_+ + (-\mu) P_-}{P_+ + P_-} = \mu \frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}} = \mu \tanh\left(\frac{\mu H}{kT}\right)$$

The magnetisation of the substance is then defined as

$$\bar{M}_0 = N_0 \bar{\mu}_H$$

↳ No interaction between atoms

Math:

$$y \ll 1 \Rightarrow \tanh y = \frac{e^y - e^{-y}}{e^y + e^{-y}} = \frac{(1+y+\dots) - (1-y+\dots)}{(1+y+\dots) + (1-y+\dots)} \approx \frac{2y}{2} = y$$

$$y \gg 1 \Rightarrow \tanh y = \frac{e^y - e^{-y}}{e^y + e^{-y}} \approx \frac{e^y}{e^y} = 1$$

There are two interesting regimes of the magnetisation

$$\bullet \quad \underbrace{\frac{\mu H}{kT} \ll 1}_{\text{high } T} : \bar{M}_0 = N_0 \cdot \mu \cdot \frac{\mu H}{kT} = N_0 \underbrace{\frac{\mu^2 H}{kT}}$$

$\chi \equiv$  magnetic

NOTE:  $\chi \propto T^{-1} \equiv$  "Curie's law"

susceptibility

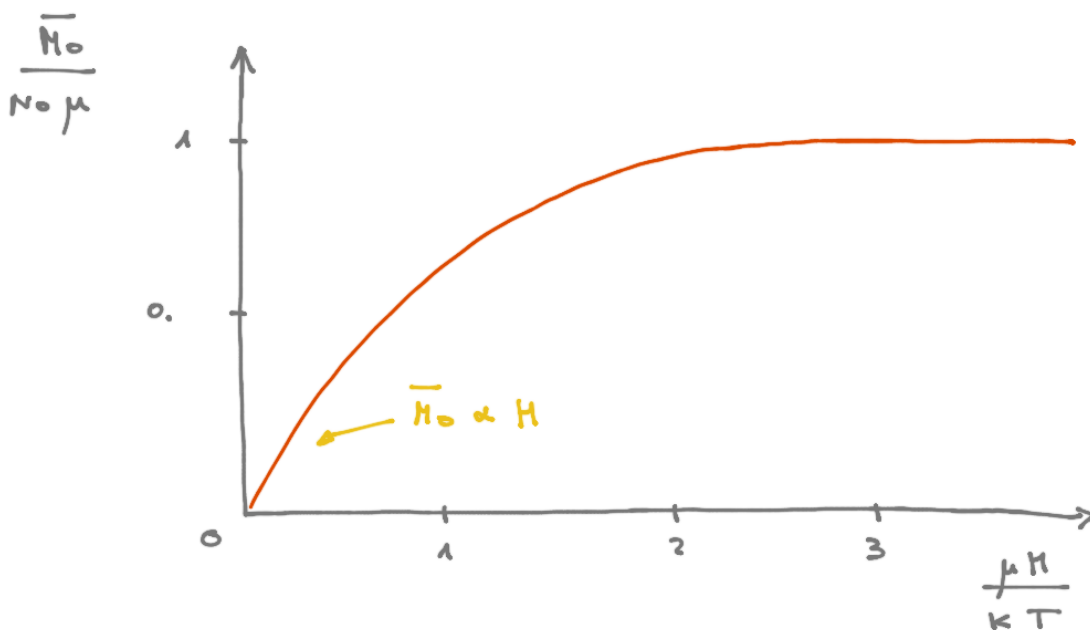
•  $\underbrace{\frac{\mu H}{kT}}_{\text{low } T} \gg 1 : \bar{M}_0 = N_0 \cdot \mu$  (independent of  $H$ )

Remark:  $T \rightarrow \infty \Rightarrow P_{\pm} \propto e^{\pm \frac{\mu H}{kT}} \sim 1 \Rightarrow |+\rangle$  and  $|-\rangle$  have same probability  
 $\Rightarrow \bar{\mu}_H \approx 0$

$T \rightarrow 0 \Rightarrow P_{+} \rightarrow 1, P_{-} \rightarrow 0 \Rightarrow |+\rangle$  is the most likely

Magnetisation curve :

$\Rightarrow \bar{\mu}_H \approx \mu$



NOTE: In order to apply the canonical ensemble we assumed

full energy  $\leftarrow$  weak interaction between the atoms and also that  
 is the sum of one atom ( $A$ ) can be distinguished from the rest ( $A'$ ).  
 over atoms



2. Molecule in an ideal gas : Let us consider a monatomic gas at temperature  $T$  confined in a volume  $V$ . We assume that the gas is very diluted so that interactions between molecules are weak (additivity of energy). We treat the problem classically so we can focus on a molecule (A) and treat the rest (A') as the heat reservoir.

$$E = \frac{1}{2} m v^2 = \frac{|\vec{p}|^2}{2m} \equiv \text{energy of a molecule}$$

Let us denote  $P(\vec{r}, \vec{p})$  the probability to find the molecule in phase space within the range  $\vec{r}$  and  $\vec{r} + d\vec{r}$  as well as  $\vec{p}$  and  $\vec{p} + d\vec{p}$ . Then

$$P(\vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} \propto \underbrace{\left( \frac{d^3\vec{r} d^3\vec{p}}{h^3} \right)}_{\text{multiplicity}} \underbrace{e^{-\beta \frac{|\vec{p}|^2}{2m}}}_{\text{Boltzmann factor}}$$

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

To find the probability  $P(\vec{p}) d^3\vec{p}$  that a particle has momentum between  $\vec{p}$  and  $\vec{p} + d\vec{p}$  irrespective of its position  $\vec{r}$  one just integrates

$$P(\vec{p}) d^3\vec{p} = \int_V P(\vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} \propto e^{-\beta \frac{|\vec{p}|^2}{2m}} d^3\vec{p}$$

or, changing variable to  $\vec{v} = \frac{\vec{p}}{m}$ , one finds

$$P(\vec{v}) d^3\vec{v} = c \underbrace{e^{-\beta \frac{m v^2}{2}}}_{\text{Gaussian}} d^3\vec{v}$$

"Maxwell distribution" [Gaussian]

NOTE:  $d^3\vec{v} \Rightarrow 4\pi v^2 dv \Rightarrow f(v) \propto v^2 e^{-\beta \frac{m v^2}{2}}$  [Non-Gaussian]

3. Molecule in an ideal gas + gravity : The system is the same as before but in the presence of gravity (in the  $-z$  direction)

$$E = \frac{|\vec{p}|^2}{2m} + m g z \equiv \text{energy of a molecule}$$

Analogously to the case before one finds

$$P(\vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} = \left( \frac{d^3\vec{r} d^3\vec{p}}{h_0^3} \right) e^{-\beta \left[ \frac{|\vec{p}|^2}{2m} + m g z \right]}$$

$$\propto d^3\vec{r} d^3\vec{p} e^{-\beta \frac{|\vec{p}|^2}{2m}} e^{-\beta m g z}$$

• Integrating over  $\vec{r}$  then

$$P(\vec{p}) d^3\vec{p} = c e^{-\beta \frac{|\vec{p}|^2}{2m}} d^3\vec{p} \quad [\text{Maxwell distribution}]$$

as for the case without gravity.

• Integrating over  $\vec{p}, x, y$  then

$$P(z) dz = c' e^{-\beta m g z} dz = \underbrace{P(0)}_{\text{"Law of atmospheres"}} e^{-\beta m g z} dz$$

#### IV. Partition function and mean values in a canonical ensemble

In this section we show how to compute mean values of quantities in the canonical ensemble

\* **Mean energy** : This is a relevant quantity because

i) A system with **specified** mean energy  $\bar{E}$  is described by a canonical ensemble  $\Rightarrow \beta$  will adapt according to

$$\bar{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}$$

ii) A system in contact with a heat reservoir with  $\beta = \frac{1}{kT}$  is described by a canonical ensemble  $\Rightarrow \bar{E}$  will adapt according to

$$\bar{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}$$

Quantum Mechanics

$$\langle f | i \rangle = \int \mathcal{D}x e^{i \frac{S}{\hbar}} = \int \mathcal{D}x e^{-\frac{S_E}{\hbar}}$$

Euclidean time  $\tau$

$t = i\tau \rightarrow \beta \equiv \frac{\tau}{\hbar}$

It is very useful to define the partition function  $Z$  as <sup>"Zustandsumme"</sup>

$$Z(\beta, x_a) = \sum_r e^{-\beta E_r(x_a)} \Rightarrow -\frac{\partial Z}{\partial \beta} = \sum_r e^{-\beta E_r} E_r$$

$\hookrightarrow$  all microstates

so that

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

We can also compute the energy dispersion  $\overline{(\Delta E)^2}$

$$\overline{(\Delta E)^2} = \overline{E^2} - \bar{E}^2 = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2 - \bar{E}^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\begin{aligned} \bar{E}^2 &= \frac{1}{Z} \sum_r e^{-\beta E_r} E_r^2 = \frac{1}{Z} \left(-\frac{\partial}{\partial \beta}\right)^2 Z = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \\ &= \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2 \end{aligned}$$

NOTE:  $\overline{(\Delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} \geq 0 \Rightarrow \frac{\partial \bar{E}}{\partial \beta} \leq 0 \Rightarrow \frac{\partial \bar{E}}{\partial T} \geq 0$

\* Mean generalised forces: Let us consider a system with one external parameter  $x$  which undergoes a quasi-static change from  $x$  to  $x + dx$ . The energy  $E_r$  of a state  $r$  changes as

$$\Delta_x E_r = \frac{\partial E_r}{\partial x} dx$$

so that

$$dW \equiv \bar{X} dx = -\left(\frac{\partial E_r}{\partial x}\right) dx = \frac{1}{Z} \sum_r e^{-\beta E_r} \left(-\frac{\partial E_r}{\partial x}\right) dx$$

$$\text{using } Z = \sum_r e^{-\beta E_r} \Rightarrow \frac{1}{Z} \left(+\frac{1}{\beta} \frac{\partial Z}{\partial x}\right) dx = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x} dx$$

$$\begin{aligned} \frac{\partial Z}{\partial x} &= \sum_r \frac{\partial Z}{\partial E_r} \frac{\partial E_r}{\partial x} \\ &= -\beta \sum_r e^{-\beta E_r} \left(\frac{\partial E_r}{\partial x}\right) \Rightarrow \boxed{\bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x}} \end{aligned}$$

NOTE: One then has that  $Z = Z(\beta, x)$ .

Ex: If  $x = V \Rightarrow Z = Z(\beta, V) \Rightarrow \bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \bar{p}(T, V)$   
 $\beta = (kT)^{-1}$   
 $\cong \text{"Equation of state"}$

### v. Canonical ensemble and connection with thermodynamics

Recall the two main quantities we have expressed in terms of the partition function  $Z(\beta, x)$ :

$$\bar{E} = - \frac{\partial \ln Z}{\partial \beta}, \quad \bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x}$$

so that

$$\begin{aligned} d \ln Z &= \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta \\ &= \beta \underbrace{\bar{X} dx}_{dW} - \bar{E} d\beta = \beta dW - \bar{E} d\beta \end{aligned}$$

Performing a "Legendre" transformation  $\bar{E} d\beta = d(\bar{E}\beta) - \beta d\bar{E}$

$$d \ln Z = \beta dW - d(\bar{E}\beta) + \beta d\bar{E}$$

$$\Rightarrow d(\ln Z + \beta \bar{E}) = \beta (dW + d\bar{E}) \equiv \beta dQ$$

↳ Definition

$$\Rightarrow d\bar{E} = \frac{1}{\beta} d(\ln Z + \beta \bar{E}) - \delta W$$

$$\underbrace{\hspace{10em}}_{\delta Q = T dS}$$

$$\Rightarrow T dS = T k d(\ln Z + \beta \bar{E})$$

$$\Rightarrow \boxed{S \equiv k (\ln Z + \beta \bar{E})} \quad \text{"Universal Gibbs entropy"} \\ \text{[valid not only at equilibrium]}$$

Since we know that  $\beta = \frac{1}{kT}$  one finds that

$$\frac{S}{k} = \ln Z + \frac{1}{kT} \bar{E} \Rightarrow \underbrace{\bar{E} - TS}_{F \text{ (Helmholtz free energy)}} = -kT \ln Z$$

$$\Rightarrow \boxed{F = -kT \ln Z = -\frac{1}{\beta} \ln Z}$$

Important : The partition function  $Z(\beta, x)$  is naturally linked to the Helmholtz free energy  $F(T, V)$  in Thermodynamics

$$\boxed{Z = e^{-\beta F}}$$

\* Connection with Boltzmann entropy formula : In a previous section we saw that

$$S = k \ln \Omega(\bar{E}) \quad \text{"Boltzmann entropy"}$$

for the entropy of a system at equilibrium with mean energy  $\bar{E}$ . Since  $\bar{E}$  is fixed the system can be described using the canonical ensemble.

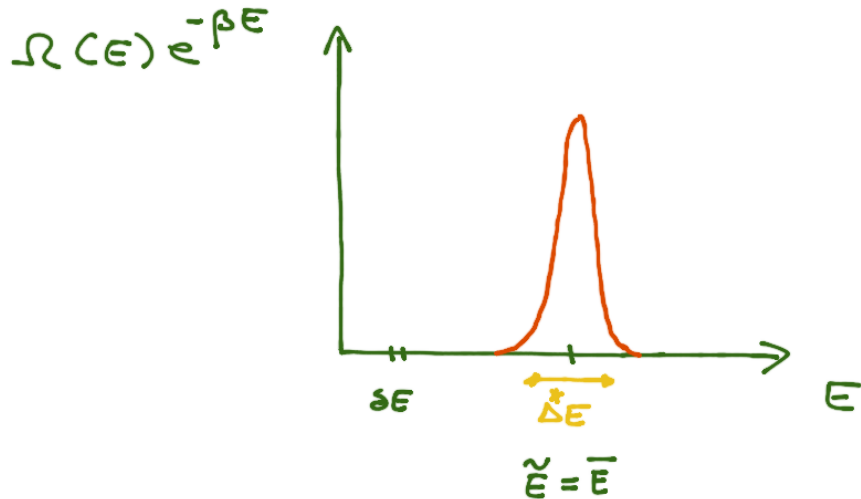
Then

Summing in two equivalent manners

$$Z = \sum_i e^{-\beta E_i} = \sum_E \Omega(E) e^{-\beta E}$$

for a system A to be in a state with energy between  $E$  and  $E + \delta E$ .

Recalling that



one can approximate

$$Z = \Omega(\bar{E}) \cdot e^{-\beta \bar{E}} \cdot \underbrace{\frac{\Delta^* E}{\delta E}}_{\# \text{ of } \delta E \text{ intervals in } \Delta^* E}$$

$$\Rightarrow \ln Z = \underbrace{\ln \Omega(\bar{E})}_{\sim f} - \underbrace{\beta \bar{E}}_{\sim f} + \underbrace{\ln \left( \frac{\Delta^* E}{\delta E} \right)}_{\sim \ln f} \approx \ln \Omega(\bar{E}) - \beta \bar{E}$$

$$\Rightarrow S = K (\ln Z + \beta \bar{E}) \stackrel{f \gg 1}{\approx} K \ln \Omega(\bar{E}) \Rightarrow \text{Boltzmann entropy recovered at equilibrium when } \underline{f \gg 1} !!$$

NOTE:  $\Omega(E) \sim E^f \Rightarrow$

- $\ln \Omega \sim f \ln E$

- $\beta E = \frac{\partial \ln \Omega}{\partial E} E \sim f$

- $\ln \left( \frac{\Delta^* E}{\delta E} \right) \sim \ln f$  (at most if all the  $f$  d.o.f are included in  $Z$ )

\* Connection with standard form of Gibbs' entropy formula: The universal Gibbs' entropy formula can be expressed in a more standard form

$$\begin{aligned}
 S &= k \left[ \ln z + \beta \bar{E} \right] = k \left[ \ln z + \beta \sum_r P_r E_r \right] \\
 &= k \left[ \ln z - \sum_r P_r \ln(z P_r) \right] \\
 &= k \left[ \ln z - \ln z \underbrace{\sum_r P_r}_1 - \sum_r P_r \ln P_r \right] \\
 &= -k \sum_r P_r \ln P_r = -k \underbrace{\overline{\ln P_r}}_{H\text{-function}} = -k H
 \end{aligned}$$

(only decreases with t)

"Standard Gibbs' entropy"

- Quantum theory  $\Rightarrow$  Von Neumann entropy
- Information theory  $\Rightarrow$  Shannon entropy

NOTE:  $P_r = \frac{e^{-\beta E_r}}{z} \Rightarrow z P_r = e^{-\beta E_r} \Rightarrow E_r = -\frac{1}{\beta} \ln(z P_r)$

Comment: If all the possible  $N$  microstates of a system are equally probable then  $P_r = \frac{1}{N}$  and then

$$S = -k \sum_{i=1}^N \frac{1}{N} \ln\left(\frac{1}{N}\right) = k N \frac{1}{N} \ln N = \underbrace{k \ln(N)}_{\text{Boltzmann entropy}}$$



\*  $T \rightarrow 0$  limit of  $Z$  and  $S_0$ : If  $T \rightarrow 0 \Leftrightarrow \beta \rightarrow \infty$   
 the only sizeable contributions to  $Z$  are those of minimal energy  $E_0 \equiv$  ground states

$$Z = \sum_r e^{-\beta E_r} \xrightarrow{\beta \rightarrow \infty} Z_0 = \underbrace{\Omega_0}_{\# \text{ ground states}} e^{-\beta E_0}$$

$$\begin{aligned} \Rightarrow S_0 &= k_B [\ln Z_0 + \beta \bar{E}] \\ &\quad \downarrow \bar{E} \rightarrow E_0 \\ &= k_B [\ln \Omega_0 - \beta E_0 + \beta E_0] \\ &= k_B \ln \Omega_0 \quad \Rightarrow \text{Third law of thermodynamics} \end{aligned}$$

Remark: Note that  $E_0 = E_0(x_\alpha)$  drops out so that  $S_0$  is independent of the parameters of the system.

\* Additivity of  $\ln Z$ ,  $\bar{E}$  and  $S$ : Let us consider two systems  $A$  and  $A'$  with microstates labelled by  $E_r$  and  $E'_s$ . If the systems are weakly interacting and reach the equilibrium

$$\begin{aligned} E_{rs}^{(0)} = E_r + E'_s &\quad \Rightarrow \quad \overset{\text{Equilibrium}}{Z^{(0)}} = \sum_{r,s} e^{-\beta E_{rs}^{(0)}} = \sum_{r,s} e^{-\beta (E_r + E'_s)} \\ &\quad \downarrow \text{weakly interacting} \\ &= \sum_{r,s} e^{-\beta E_r} \cdot e^{-\beta E'_s} = \underbrace{\left( \sum_r e^{-\beta E_r} \right)}_Z \underbrace{\left( \sum_s e^{-\beta E'_s} \right)}_{Z'} \end{aligned}$$

Therefore

$$z^{(0)} = z \cdot z' \Rightarrow \ln z^{(0)} = \ln z + \ln z'$$

and

$$\begin{aligned}\overline{E}^{(0)} &= \frac{1}{z^{(0)}} \sum_{i,s} E_{i,s}^{(0)} e^{-\beta E_{i,s}^{(0)}} = \frac{1}{z^{(0)}} \sum_{i,s} (E_i + E'_s) e^{-\beta E_i} \cdot e^{-\beta E'_s} \\ &= \frac{1}{z^{(0)}} \sum_i E_i e^{-\beta E_i} \underbrace{\sum_s e^{-\beta E'_s}}_{z'} + \frac{1}{z^{(0)}} \sum_s E'_s e^{-\beta E'_s} \underbrace{\sum_i e^{-\beta E_i}}_z \\ &= \frac{1}{z} \sum_i E_i e^{-\beta E_i} + \frac{1}{z'} \sum_s E'_s e^{-\beta E'_s} = \overline{E} + \overline{E}'\end{aligned}$$

NOTE: Alternatively, since  $\overline{E} = \frac{\partial \ln z}{\partial \beta}$  and  $\ln z$  is additive, one readily has  $\overline{E}^{(0)} = \overline{E} + \overline{E}'$ .

It then follows that

$$\begin{aligned}S^{(0)} &= \kappa [\ln z^{(0)} + \beta \overline{E}^{(0)}] = \kappa \cdot [\ln z + \beta \overline{E}] + \kappa [\ln z' + \beta \overline{E}'] \\ &= S + S'\end{aligned}$$

$\Rightarrow$  Extensive thermodynamics functions of weakly interacting systems are additive.

\* Systems separately in equilibrium: let us consider two systems A and A' separately in equilibrium with temperatures  $\beta = \frac{1}{kT}$  and  $\beta' = \frac{1}{kT'}$ . Then

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}, \quad P'_s = \frac{e^{-\beta' E'_s}}{\sum_s e^{-\beta' E'_s}}$$

If A and A' are weakly interacting under thermal contact then their respective probabilities are statistically independent and

$$\underbrace{P_{rs}^{(0)}}_{\substack{\text{A in state } r \\ \text{A' in state } s}} = P_r \cdot P'_s = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \frac{e^{-\beta' E'_s}}{\sum_s e^{-\beta' E'_s}}$$

$$\Rightarrow \underbrace{P_{rs}^{(0)}}_{\text{only if } \underline{\beta = \beta'}} = \frac{e^{-\beta(E_r + E'_s)}}{\underbrace{\sum_{rs} e^{-\beta(E_r + E'_s)}}_{\text{Canonical distribution}}}$$

\* Important 1: The canonical ensemble implies all the thermodynamic relations of statistical thermodynamics.

\* Important 2: The definition  $S = k [\ln Z + \beta \bar{E}]$  is very convenient since it requires the knowledge of  $Z$  rather than  $\Omega$ .

i)  $z = \sum_r e^{-\beta E_r} \Rightarrow$  Unrestricted sum over all states  
 $\Rightarrow$  Directly computable from Hamiltonian

ii)  $\Omega \Rightarrow$  Restricted count of microstates with energy  
 between  $E$  and  $E + \delta E \Rightarrow$  Dependence on  $\delta E$

## vi. Mathematical derivation of the canonical ensemble

Let us re-derive the canonical distribution in a much more abstract and general manner. Let us consider a system  $A$  with known mean energy  $\bar{E}$ .

Representative ensemble: Large number  $a \gg 1$  of copies,  $a_r$  of which are in a state  $r$  with  $E_r$ .  
 Then  $P_r = \frac{a_r}{a}$  and:

$$\sum_r a_r = a, \quad \sum_r P_r E_r = \frac{1}{a} \sum_r a_r E_r = \bar{E}$$

The number  $\Gamma$  of different ways of distributing  $a_1$  copies in  $r=1$ ,  $a_2$  copies in  $r=2$ , etc. is given by

$$\Gamma = \frac{a!}{a_1! a_2! a_3! \dots} \Rightarrow \ln \Gamma = \ln a! - \sum_r \ln a_r!$$

$$\approx a \ln a - a - \sum_r a_r \ln a_r + \underbrace{\sum_r a_r}_a$$

$$= a \ln a - \sum_r a_r \ln a_r$$

NOTE: (Stirling approximation)  $\ln a_r! \approx a_r \ln a_r - a_r + \frac{1}{2} \ln(2\pi a_r)$   
 $a_r \gg 1$  negligible

Question: Which are the values of  $a_r$  maximising  $\Gamma(a_r)$ ?

$$\begin{aligned} \delta \ln \Gamma &= \delta \left[ a \ln a - \sum_r a_r \ln a_r \right] = - \delta \left[ \sum_r a_r \ln a_r \right] \\ &= - \sum_r \delta a_r \ln a_r - \sum_r a_r \frac{1}{a_r} \delta a_r \\ &= - \sum_r \ln a_r \delta a_r - \sum_r \delta a_r = 0 \end{aligned}$$

Since

$$\rightarrow dq_1 = \sum_r 1 da_r = 0$$

Constraints  $\left\{ \begin{array}{l} \sum_r a_r = a \Rightarrow \sum_r \delta a_r = 0 \\ \frac{1}{a} \sum_r a_r E_r = \bar{E} \Rightarrow \sum_r a_r E_r = a \bar{E} \Rightarrow \sum_r E_r \delta a_r = 0 \end{array} \right.$

$\rightarrow \bar{E} = \text{fixed}$   $\uparrow$   $dq_2 = \sum_r E_r da_r = 0$

$\hookrightarrow$  indep of  $a_r$

one finds

$$\delta \ln \Gamma = - \sum_r \ln a_r \delta a_r$$

not all of them are independent  $\Leftrightarrow$  2 constraints  
 $\Rightarrow$  Lagrange multipliers

We then introduce the 2 constraints by means of 2 Lagrange multipliers  $(\alpha, \beta)$  so that

$$- \sum_r \left( \underbrace{\ln a_r}_{d \ln \Omega} + \underbrace{\gamma}_{\text{now they are independent}} \times \underbrace{1}_{dq_1} + \beta \times \underbrace{E_r}_{dq_2} \right) \delta a_r = 0$$

Solving this equation provides the maximum at  $a_r = \tilde{a}_r$  given by

$$\ln \tilde{a}_r + \gamma + \beta E_r = 0 \Rightarrow \tilde{a}_r = e^{-\gamma} \cdot e^{-\beta E_r}$$

The Lagrange multipliers  $(\gamma, \beta)$  are now determined by requiring that the 2 constraints hold

$$\bullet \sum_r \tilde{a}_r = a \Rightarrow e^{-\gamma} \sum_r e^{-\beta E_r} = a \Rightarrow e^{-\gamma} = a \left( \sum_r e^{-\beta E_r} \right)^{-1}$$

$$\bullet \frac{1}{a} \sum_r \tilde{a}_r E_r = \bar{E} \Rightarrow \frac{\sum_r \tilde{a}_r E_r}{\sum_r \tilde{a}_r} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = \bar{E}$$

$$\Rightarrow \tilde{p}_r \equiv \frac{\tilde{a}_r}{a} = \frac{\tilde{a}_r}{\sum_r \tilde{a}_r} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

"Canonical ensemble"

[Maximise  $\ln \Omega$ ]

2 constraints : normalisation +  $\bar{E}$

Let us now re-express  $\ln \Omega$  using  $p_r \equiv \frac{a_r}{a}$  as

$$\ln \Omega = a \ln a - \sum_r a_r \ln a_r = a \ln a - \sum_r (a p_r) \ln (a p_r)$$

$$\begin{aligned}
&= a \ln a - a \sum_r P_r (\ln a + \ln P_r) \\
&= a \ln a - a \ln a \overbrace{\sum_r P_r}^1 - \sum_r a P_r \ln P_r \\
&= -a \sum_r P_r \ln P_r
\end{aligned}$$

so that  $\ln \Omega$  is maximised for  $P_r \equiv$  Canonical distribution and then

$$\ln \tilde{\Omega} = -a \sum_r \tilde{P}_r \ln \tilde{P}_r = \frac{a}{k} S$$

NOTE: Recall that in the canonical ensemble we have the standard Gibbs entropy  $S = -k \sum_r P_r \ln P_r = -k \overline{\ln P_r}$

MESSAGE: Canonical ensemble maximises Gibbs entropy when  $\bar{E}$  = fixed

Important: An increase of  $\ln \tilde{\Omega}$  implies a more random distribution of copies over available states  $\Rightarrow$  a loss of information about the distribution of copies over available states.

Important: The maximum value  $\ln \tilde{\Omega}$  gives the entropy of the final equilibrium state

Remark: The quantity  $-\sum_r P_r \ln P_r$  is a measure of randomness  $\Rightarrow + \sum_r P_r \ln P_r$  is a measure of non-randomness in information theory

## vii. System with specified $\bar{E}$ and $\bar{N}$ ( $V = \text{fixed}$ ): Grand canonical ensemble

This ensemble is used to describe systems with **fixed volume  $V$**  but an **indefinite number of particles and energy**. In other words, neither the energy  $E$  nor the number of particles  $N$  of the system  $A$  are fixed but fluctuate (although their mean values are fixed)

We follow the same construction as for the canonical ensemble and put  $A$  in contact with a **reservoir  $A'$**  such that  $A \ll A'$ . Then ↳ of heat and particles

$$A^{(0)} = A + A' \Rightarrow \begin{cases} E + E' = E^{(0)} = \text{cte} \\ N + N' = N^{(0)} = \text{cte} \end{cases}$$



As for the canonical ensemble one has now that

$$P_r(E_r, N_r) \propto \Omega'(E^{(0)} - E_r, N^{(0)} - N_r)$$

with  $E_r \ll E^{(0)}$  and  $N_r \ll N^{(0)}$ . Taylor expanding around  $E^{(0)}$

$$\ln \Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \ln \Omega'(E^{(0)}, N^{(0)}) - \overbrace{\frac{\partial \ln \Omega'}{\partial E}}^{\beta} \Big|_0 E_r - \overbrace{\frac{\partial \ln \Omega'}{\partial N}}^{\alpha} \Big|_0 N_r$$

$$\Rightarrow \Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \Omega'(E^{(0)}, N^{(0)}) \cdot e^{-\beta E_r - \alpha N_r}$$

"Grand canonical ensemble"  $\Rightarrow$

$$P_r = \frac{e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}$$



$\mu = \text{energy/particle}$   $\leftarrow$   $[\mu] = [E]$   $\leftrightarrow$  chemical potential  
 Redefining  $\beta \equiv \frac{1}{kT}$  and  $\alpha \equiv -\beta\mu = -\frac{\mu}{kT}$ , these are  
 specified by demanding sign to meet convention:  $d\bar{E} = TdS - \bar{P}dV + \mu d\bar{N}$

$$\bar{E} = \frac{\sum_r E_r e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}, \quad \bar{N} = \frac{\sum_r N_r e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

where the sum is over all the possible states of the system.

\* Grand canonical partition function: It is then defined as

$$\mathcal{Z}(\beta, \mu, \alpha) = \sum_r e^{\frac{\mu N_r - E_r}{kT}} = \sum_r e^{-\beta(E_r - \mu N_r)} = \sum_r e^{-\beta E_r} z^{N_r}$$

with  $e^{\frac{\mu}{kT}} = e^{\beta\mu} \equiv z \equiv \text{fugacity}$

\* Mean energy  $\bar{E}$  and number of particles  $\bar{N}$ : These are relevant quantities because

i) A system with specified mean energy  $\bar{E}$  and mean number of particles  $\bar{N}$  is described by a grand canonical ensemble  $\Rightarrow \beta$  and  $\mu$  will adopt according to

$$\bar{E} = \frac{\sum_r e^{-\beta(E_r - \mu N_r)} E_r}{\sum_r e^{-\beta(E_r - \mu N_r)}}, \quad \bar{N} = \frac{\sum_r e^{-\beta(E_r - \mu N_r)} N_r}{\sum_r e^{-\beta(E_r - \mu N_r)}}$$

ii) A system in contact with a heat and particles reservoir with  $\beta = \frac{1}{kT}$  and  $\mu = -\frac{\alpha}{\beta}$  is described by a grand canonical ensemble  $\Rightarrow \bar{E}$  and  $\bar{N}$  will adapt according to

$$\bar{E} = \frac{\sum_r e^{-\beta(E_r - \mu N_r)} E_r}{\sum_r e^{-\beta(E_r - \mu N_r)}}, \quad \bar{N} = \frac{\sum_r e^{-\beta(E_r - \mu N_r)} N_r}{\sum_r e^{-\beta(E_r - \mu N_r)}}$$

In terms of the partition function

$$\mathcal{Z}(\beta, \mu, x) = \sum_r e^{-\beta(E_r - \mu N_r)} = \sum_r e^{-\beta E_r - \alpha N_r}$$

one has that

$$\bar{E} - \mu \bar{N} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}, \quad \bar{N} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \alpha} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$$

or  $\bar{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \mu} \underbrace{\left(\frac{\partial \mu}{\partial \alpha}\right)}_{\mu = -\frac{\alpha}{\beta}} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$

\* Mean generalised forces: Let us consider a system with one external parameter  $x$  which undergoes a quasi-static change from  $x$  to  $x+dx$ . The energy  $E_r$  and number of particles  $N_r$  of a state  $r$  change as

$$\Delta_x E_r = \frac{\partial E_r}{\partial x} dx \quad \text{and} \quad \Delta_x N_r = \frac{\partial N_r}{\partial x} dx$$

Let us focus on mechanical interaction  $[dQ=0]$  for a specific microstate  $r$ . As we saw before, when the system remains in the state  $r$  it performs an amount of work

$$dW_r \equiv -dE_r = -\underbrace{\mu}_{\text{pulled out}} dN_r + \underbrace{dW_r}_{\text{mechanical work}}$$

change in  
measurable  
external parameters  
 $x_\alpha = V, \dots$

$$\Rightarrow dW_r = -dE_r + \mu dN_r$$

$$= \sum_{\alpha=1}^n \left( -\frac{\partial E_r}{\partial x_\alpha} + \mu \frac{\partial N_r}{\partial x_\alpha} \right) dx_\alpha$$

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

so that (only one external parameter  $x$ )

$$dW \equiv \overline{X} dx = \overline{\left( -\frac{\partial E_r}{\partial x} + \underbrace{\mu}_{\mu = -\alpha k T} \frac{\partial N_r}{\partial x} \right)} dx$$

reservoir  
temperature

$$= \frac{\partial}{\partial x} [-E_r + \mu N_r] dx$$

$$= \frac{1}{Z} \sum_r e^{-\beta(E_r - \mu N_r)} \frac{\partial}{\partial x} [-E_r + \mu N_r] dx$$

$$\text{using } Z = \sum_r e^{-\beta(E_r - \mu N_r)} \Rightarrow = \frac{1}{Z} \left( \frac{1}{\beta} \frac{\partial Z}{\partial x} \right) dx = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x} dx$$

$$\frac{\partial Z}{\partial x} = \frac{\partial Z}{\partial E_r} \frac{\partial E_r}{\partial x} + \frac{\partial Z}{\partial N_r} \frac{\partial N_r}{\partial x} = \beta \sum_r e^{-\beta(E_r - \mu N_r)} \frac{\partial}{\partial x} [-E_r + \mu N_r]$$

$$\Rightarrow \boxed{\bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x}}$$

NOTE: One then has that  $Z = Z(\beta, \mu, x)$

$$\text{Ex: If } x = V \Rightarrow Z = Z(\beta, \mu, x) \Rightarrow \bar{P} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \bar{P}(T, \mu, V)$$

$\beta = (kT)^{-1}$

$\cong \text{ "Equation of state"}$

If the system can also exchange heat [ $dQ \neq 0$ ] one has the 1<sup>st</sup> law of thermodynamics

$$d\bar{E} = dQ - dW = TdS + \mu d\bar{N} - \underbrace{\delta W}_{\text{mechanical work}}$$

$$\Rightarrow d\bar{E} = TdS + \mu d\bar{N} - \bar{P} dV \Rightarrow \bar{E} = \bar{E}(S, \bar{N}, V)$$

$x = \text{volume } V$       Maxwell relations:  $T = \left( \frac{\partial \bar{E}}{\partial S} \right), \mu = \left( \frac{\partial \bar{E}}{\partial \bar{N}} \right), -\bar{P} = \left( \frac{\partial \bar{E}}{\partial V} \right)$

## viii. Grand canonical ensemble and connection with thermodynamics

Recall the three main quantities we have expressed in terms of the partition function  $\mathcal{Z}(\beta, \mu, x)$

$$\bar{E} - \mu \bar{N} = - \frac{\partial \ln \mathcal{Z}}{\partial \beta}, \quad \bar{N} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}, \quad \bar{X} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial x}$$

so that

$$\begin{aligned} d \ln \mathcal{Z} &= \frac{\partial \ln \mathcal{Z}}{\partial x} dx + \frac{\partial \ln \mathcal{Z}}{\partial \beta} d\beta + \frac{\partial \ln \mathcal{Z}}{\partial \mu} d\mu \\ &= \beta \underbrace{\bar{X} dx}_{\delta W} - \bar{E} d\beta + \mu \bar{N} d\beta + \beta \bar{N} d\mu \end{aligned}$$

Performing two "Legendre" transformations

$$\bar{E} d\beta = d(\bar{E}\beta) - \beta d\bar{E}$$

$$\mu \bar{N} d\beta + \beta \bar{N} d\mu = d(\beta \bar{N} \mu) - \beta \mu d\bar{N}$$

then

$$d \ln \mathcal{Z} = \beta \delta W - d(\bar{E}\beta) + \beta d\bar{E} + d(\beta \bar{N} \mu) - \beta \mu d\bar{N}$$

$$\Rightarrow d \left[ \ln \mathcal{Z} + \beta (\bar{E} - \mu \bar{N}) \right] = \beta \underbrace{(d\bar{E} + \delta W - \mu d\bar{N})}_{\delta W} \equiv \beta \delta Q \quad \hookrightarrow \text{Definition}$$

$$\Rightarrow d\bar{E} = \underbrace{\frac{1}{\beta} d[\ln \mathcal{Z} + \beta(\bar{E} - \mu \bar{N})]}_{dQ = TdS} - dW$$

$$\Rightarrow TdS = kT d[\ln \mathcal{Z} + \beta(\bar{E} - \mu \bar{N})]$$

$$\Rightarrow \boxed{S \equiv k [\ln \mathcal{Z} + \beta(\bar{E} - \mu \bar{N})]} \quad \text{"Universal Gibbs formula"}$$

Since we know that  $\beta = \frac{1}{kT}$  one finds that

$$\frac{S}{k} = \ln \mathcal{Z} + \frac{1}{kT} (\bar{E} - \mu \bar{N}) \Rightarrow \underbrace{\bar{E} - \mu \bar{N} - TS}_{\Phi \equiv \text{Grand potential or Landau potential}} = -kT \ln \mathcal{Z}$$

$$\Rightarrow \Phi = -kT \ln \mathcal{Z} = -\frac{1}{\beta} \ln \mathcal{Z}$$

Important : The partition function  $\mathcal{Z}(\beta, \mu, x)$  is naturally linked to the grand potential  $\Phi(\beta, \mu, x)$  in Thermodynamics

$$\boxed{\mathcal{Z} = e^{-\beta \Phi}}$$

\* Connection with Boltzmann entropy formula: Since  $\bar{E}$  and  $\bar{N}$  are fixed we will consider the grand canonical ensemble

$$Z = \sum_r e^{-\beta(E_r - \mu N_r)} = \sum_r e^{-\beta E_r} z^{N_r}$$

for a system A to be in a state with energy between E and  $E + \delta E$  and number of particles between N and  $N + \delta N$ .

By virtue again of the sharpness of  $\Omega(E, N) \cdot e^{-\beta E} \cdot z^N$  we can approximate

$$Z \approx \Omega(\bar{E}, \bar{N}) \cdot e^{-\beta \bar{E}} \cdot z^{\bar{N}} \cdot \left( \frac{\delta E}{\delta E} \right) \cdot \left( \frac{\delta N}{\delta N} \right)$$

$$\Rightarrow \ln Z = \underbrace{\ln \Omega(\bar{E}, \bar{N})}_{\sim f} - \underbrace{\beta \bar{E}}_{\sim f} + \underbrace{\bar{N} \ln z}_{\sim \bar{N} \sim f} + \underbrace{\ln \left( \frac{\delta E}{\delta E} \right)}_{\sim \ln f} + \underbrace{\ln \left( \frac{\delta N}{\delta N} \right)}_{\sim \ln f}$$

$$\approx \ln \Omega(\bar{E}, \bar{N}) - \beta \bar{E} + \beta \mu \bar{N}$$

$$\Rightarrow S = k_B [\ln Z + \beta \bar{E} - \beta \mu \bar{N}] \approx k_B \ln \Omega(\bar{E}, \bar{N}) \Rightarrow \text{Boltzmann entropy at equilibrium}$$

$f \gg 1$

\* Connection with standard form of Gibbs' entropy formula: We proceed as for the canonical ensemble

$$\begin{aligned}
 S &= k [\ln \mathcal{Z} + \beta (\bar{E} - \mu \bar{N})] = k [\ln \mathcal{Z} + \beta \sum_r P_r (E_r - \mu N_r)] \\
 &= k [\ln \mathcal{Z} - \sum_r P_r \ln (\mathcal{Z} P_r)] \\
 &= k [\ln \mathcal{Z} - \underbrace{\ln \mathcal{Z} \sum_r P_r}_{1} - \sum_r P_r \ln P_r] \\
 &= -k \sum_r P_r \ln P_r = -k \underbrace{\ln P_r}_{H\text{-function}} = -k H
 \end{aligned}$$

(only decreases with time)

NOTE:  $P_r = \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}} \Rightarrow \mathcal{Z} P_r = e^{-\beta(E_r - \mu N_r)}$

$$\Rightarrow (E_r - \mu N_r) = -\frac{1}{\beta} \ln (\mathcal{Z} P_r)$$

\* Mathematical derivation of the grand canonical ensemble: Let us rederive the grand canonical ensemble in an abstract manner. Let us consider a system A with known mean energy  $\bar{E}$  and number of particles  $\bar{N}$ .

Representative ensemble: large number  $a \gg 1$  of copies,  $a_r$  of which are in a state  $r$  with  $(E_r, N_r)$



Then

$$\sum_r a_r = a, \quad \frac{1}{a} \sum_r a_r E_r = \bar{E}, \quad \frac{1}{a} \sum_r a_r N_r = \bar{N}$$

The number  $\Gamma$  of different ways of distributing  $a_1$  copies in  $r=1$ ,  $a_2$  copies in  $r=2$ , etc. is given by

$$\begin{aligned} \Gamma &= \frac{a!}{a_1! a_2! a_3! \dots} \Rightarrow \ln \Gamma = \ln a! - \sum_r \ln a_r! \\ &\approx a \ln a - a - \sum_r a_r \ln a_r + \underbrace{\sum_r a_r}_a \\ &= a \ln a - \sum_r a_r \ln a_r \end{aligned}$$

NOTE: (Stirling approximation)  $\ln a_r! \underset{a_r \gg 1}{\approx} a_r \ln a_r - a_r + \underbrace{\frac{1}{2} \ln(2\pi a_r)}_{\text{negligible}}$

Question: Which are the values of  $a_r$  maximising  $\Gamma(a_r)$ ?

$$\begin{aligned} \delta \ln \Gamma &= \delta \left[ a \ln a - \sum_r a_r \ln a_r \right] = - \delta \left[ \sum_r a_r \ln a_r \right] \\ &= - \sum_r \delta a_r \ln a_r - \sum_r a_r \frac{1}{a_r} \delta a_r \\ &= - \sum_r \ln a_r \delta a_r - \sum_r \delta a_r = 0 \end{aligned}$$

Since this true there are three constraints

Constraints

$$\left\{ \begin{array}{l} \sum_r a_r = a \Rightarrow \sum_r \delta a_r = 0 \rightarrow dg_1 = \sum_r 1 da_r = 0 \\ \frac{1}{a} \sum_r a_r E_r = \bar{E} \Rightarrow \sum_r a_r E_r = a \bar{E} \Rightarrow \sum_r E_r \delta a_r = 0 \\ \frac{1}{a} \sum_r a_r N_r = \bar{N} \Rightarrow \sum_r a_r N_r = a \bar{N} \Rightarrow \sum_r N_r \delta a_r = 0 \end{array} \right.$$

↑ indep of  $a_r$

$$\rightarrow dg_2 = \sum_r E_r da_r = 0, \quad dg_3 = \sum_r N_r da_r = 0$$

one finds

$$\delta \ln \Gamma = - \sum_r \ln a_r \delta a_r$$

not all of them are independent  $\Leftrightarrow$  3 constraints  
 $\Rightarrow$  Lagrange multipliers

We then introduce the 3 constraints by means of 3 Lagrange multipliers  $(\gamma, \beta, \alpha)$  so that

$$- \sum_r \left( \underbrace{\ln a_r}_{d \ln \Gamma} + \underbrace{\gamma \times 1}_{dg_1} + \underbrace{\beta \times E_r}_{dg_2} + \underbrace{\alpha \times N_r}_{dg_3} \right) \delta a_r = 0$$

now they are indep.

Solving this equation provides the maximum at  $a_r = \tilde{a}_r$  given by

$$\ln \tilde{a}_r + \gamma + \beta E_r + \alpha N_r = 0 \Rightarrow \tilde{a}_r = e^{-\gamma} \cdot e^{-\beta E_r - \alpha N_r}$$

The Lagrange multipliers  $(\gamma, \beta, \alpha)$  are now determined by requiring that the 3 constraints hold

$$\bullet \sum_r \tilde{a}_r = a \Rightarrow e^{-\gamma} \sum_r e^{-\beta E_r - \alpha N_r} = a \Rightarrow e^{-\gamma} = a \left( \sum_r e^{-\beta E_r - \alpha N_r} \right)^{-1}$$

$$\bullet \frac{1}{a} \sum_r \tilde{a}_r E_r = \bar{E} \Rightarrow \frac{\sum_r \tilde{a}_r E_r}{\sum_r \tilde{a}_r} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} E_r}{\sum_r e^{-\beta E_r - \alpha N_r}} = \bar{E}$$

$$\bullet \frac{1}{a} \sum_r \tilde{a}_r N_r = \bar{N} \Rightarrow \frac{\sum_r \tilde{a}_r N_r}{\sum_r \tilde{a}_r} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} N_r}{\sum_r e^{-\beta E_r - \alpha N_r}} = \bar{N}$$

$$\Rightarrow \tilde{p}_r \equiv \frac{\tilde{a}_r}{a} = \frac{\tilde{a}_r}{\sum_r \tilde{a}_r} = \frac{e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}} \quad \text{"Grand canonical ensemble"}$$

[ Maximise  $\ln \Gamma$  ]

3 constraints : normalisation +  $\bar{E}$  +  $\bar{N}$

Let us now recall that  $\ln \Gamma$  can be expressed as

$$\ln \Gamma = a \ln a - \sum_r a_r \ln a_r = a \ln a - \sum_r (a p_r) \ln (a p_r)$$

$$p_r \equiv \frac{a_r}{a}$$

$$= a \ln a - a \sum_r p_r (\ln a + \ln p_r) = a \ln a - a \ln a \underbrace{\sum_r p_r}_1 - a \sum_r p_r \ln p_r$$

$$= -a \sum_r p_r \ln p_r$$

so that  $\ln \Gamma$  is maximised for  $p_r \equiv$  Grand canonical distribution and

then

$$\ln \tilde{\Gamma} = -a \sum_r \tilde{p}_r \ln \tilde{p}_r = \frac{a}{k} S$$

MESSAGE : Grand canonical ensemble maximises Gibbs entropy when  $\bar{E}, \bar{N}$  = fixed

\* Thermodynamic potentials: Starting from the internal energy

$$d\bar{E} = T dS - \bar{p} dV + \mu d\bar{N}$$

and performing Legendre transformations we find the rest of the thermodynamic potentials:

$$\bullet dH = d(\bar{E} + \bar{p}V) = T dS + V d\bar{p} + \mu d\bar{N} \equiv dH(S, \bar{p}, \bar{N})$$

$$\bullet dG = d(H - TS) = -S dT + V d\bar{p} + \mu d\bar{N} \equiv dG(T, \bar{p}, \bar{N})$$

$$\bullet dF = d(\bar{E} - TS) = -S dT - \bar{p} dV + \mu d\bar{N} \equiv dF(T, V, \bar{N})$$

$$\bullet d\Phi = d(F - \mu\bar{N}) = -S dT - \bar{p} dV - \bar{N} d\mu \equiv d\Phi(T, V, \mu)$$

\* Connection with canonical ensemble if  $N_r = N = \text{fixed}$ : If the number of particles  $N_r$  is the same in all the states  $r$  then

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N)} = e^{\beta \mu N} \sum_r e^{-\beta E_r} = z^N \mathcal{Z}(\beta, x)$$

$$\Rightarrow P_r = \frac{z^N e^{-\beta E_r}}{\mathcal{Z}} = \frac{e^{-\beta E_r}}{z} \Rightarrow \text{"canonical distribution"}$$

~~~~~
grand canonical

Moreover  $\mu = \left( \frac{\partial \bar{E}}{\partial \bar{N}} \right)_{S, V} = 0$  and  $\Phi = F$ .

$$\hookrightarrow \bar{E} = \sum_r P_r E_r \neq \bar{E}(N)$$

↑ indep. of  $N = \bar{N}$

\* Alternative expression for  $\mathcal{Z}(\beta, \mu, x)$ : The grand canonical partition function can be expressed alternatively as

$$\mathcal{Z}(\beta, \mu, x) = \sum_r e^{-\beta(E_r - \mu N_r)}$$

$$\text{(see Ex)} = \sum_N e^{\beta \mu N} \sum_{j_N} e^{-\beta E_{j_N}}$$

$$= \sum_N \underbrace{z^N}_{\text{fugacity}} \underbrace{Z_N(\beta, x)}_{\text{Canonical partition function for these states with } N \text{ particles}}$$

fugacity Canonical partition function for these states with  $N$  particles

Ex: let us consider a system with

|         |       |       |       |       |       |       |       |       |       |     |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----|
| $r =$   | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | ... |
| $E_r =$ | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $E_5$ | $E_6$ | $E_7$ | $E_8$ | $E_9$ | ... |
| $N_r =$ | 3     | 1     | 1     | 3     | 2     | 1     | 3     | 3     | 2     | ... |

so that

$$\begin{aligned} \mathcal{Z} &= \sum_r e^{-\beta(E_r - \mu N_r)} = \sum_r e^{\beta \mu N_r} e^{-\beta E_r} = \sum_r z^{N_r} e^{-\beta E_r} \\ &= z^1 [e^{-\beta E_2} + e^{-\beta E_3} + e^{-\beta E_6} + \dots] + z^2 [e^{-\beta E_5} + e^{-\beta E_9} + \dots] \\ &+ z^3 [e^{-\beta E_1} + e^{-\beta E_4} + e^{-\beta E_7} + e^{-\beta E_8} + \dots] = \sum_N z^N Z_N(\beta, x) \end{aligned}$$

## Appendix: Constrained systems and Lagrange multipliers

The problem is that of extremising  $f(x_1, x_2, \dots, x_n)$  where the variables  $x_n$  are not independent and obey

$$g(x_1, x_2, \dots, x_n) = 0 \Rightarrow \underbrace{\frac{\partial g}{\partial x_1} dx_1 + \frac{\partial g}{\partial x_2} dx_2 + \dots + \frac{\partial g}{\partial x_n} dx_n}_{= 0} = 0$$

We can solve for  $dx_n$  as a

we will refrain from doing this!!  $\Leftarrow$  function of  $dx_1, dx_2, \dots, dx_{n-1}$   
[not all  $dx_i$  are independent]

The extremisation of  $f(x_1, \dots, x_n)$  reduces to

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots + \frac{\partial f}{\partial x_n} dx_n = 0$$

but one also has that

$$\lambda dg = \lambda \frac{\partial g}{\partial x_1} dx_1 + \lambda \frac{\partial g}{\partial x_2} dx_2 + \dots + \lambda \frac{\partial g}{\partial x_n} dx_n = 0$$

so

$$df + \lambda dg = \left( \frac{\partial f}{\partial x_1} + \lambda \frac{\partial g}{\partial x_1} \right) dx_1 + \dots + \left( \frac{\partial f}{\partial x_n} + \lambda \frac{\partial g}{\partial x_n} \right) dx_n = 0 \quad (i)$$

but NOT all the  $dx_i$  are independent

Now is when Lagrange's trick comes in ...

1) Choose one specific  $dx_i$ , i.e.  $dx_n$ , and adjust  $\lambda$  such that

$$\frac{\partial f}{\partial x_n} + \lambda \frac{\partial g}{\partial x_n} = 0$$

2) As a result, only  $dx_1, \dots, dx_{n-1}$  survive which are also independent so that (i) requires

$$\frac{\partial f}{\partial x_i} + \lambda \frac{\partial g}{\partial x_i} = 0 \quad \text{with } i=1, \dots, n-1$$

3) Therefore the net result of this argument is that

$$\frac{\partial f}{\partial x_i} + \lambda \frac{\partial g}{\partial x_i} = 0 \quad \text{for } \underline{\underline{\text{all}}} \ i=1, \dots, n$$

$\Rightarrow$  All  $dx_i$  ( $i=1, \dots, n$ ) in (i) can be viewed as independent at expenses of postponing the determination of  $\lambda$  as the solution  $\vec{x}_0 = (x_1, \dots, x_n) \equiv \text{extremum}$  will depend on  $\lambda \Rightarrow \vec{x}_0(\lambda)$

\* The "Lagrange multiplier  $\lambda$ " will be determined by requiring

$$g(\vec{x}_0) = 0 \quad [\text{original constraint}]$$

$\hookrightarrow$  Condition for  $\lambda$  !!