

Paradoxical mixing

L0

① Description of a gas

Γ -space, Distinguishability, Equilibrium

② Entropy (Gibbs) and 2nd law

Gibbs entropy, 2nd law, Time arrow.

③ Entropy (Boltzmann)

$S = k_B \ln W$, 2nd law (bis), Preferential time arrow.

④ Two experiments of Paradoxical Mixing.
(cf. slides + videos)

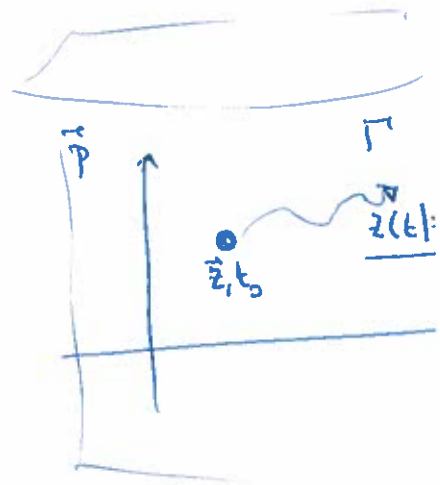
⑤ Add-on: Gibbs vs Boltzmann.

① Description of a gas:

Microscopic: Assemblies of N objects, whose microscopic evolution could in principle be fully predicted by a Hamiltonian $H_N(\vec{p}, \vec{q}, t)$
 $n = 3N$

Isolated gas: $H_N(\vec{q}, \vec{p}, t)$.

Γ -space: $\left\{ (\vec{p}, \vec{q}) \in \mathbb{R}^{3N} \times \mathbb{R}^{3N} \right\}$
 1 point in Γ -space = position, velocities of every N molecule



Observational state: We assume that while the microscopic dynamics is in principle fully deterministic, a perfect specification of the system is not only non-reachable but also non-physical. The best that one can achieve is to measure " Γ -space configurations", which means to analyze

the state of the gas at time t up to
$$\underline{h^N = \prod_{i=1}^N (\Delta p_i \Delta q_i)}$$

We can therefore think of Γ -space in terms of a countable partition of Γ -cells $\Gamma_1, \dots, \Gamma_k$ of size $|\Gamma_i| = \Delta p^N \Delta q^N$.

At this point it is necessary to make the distinction between two types of gas.

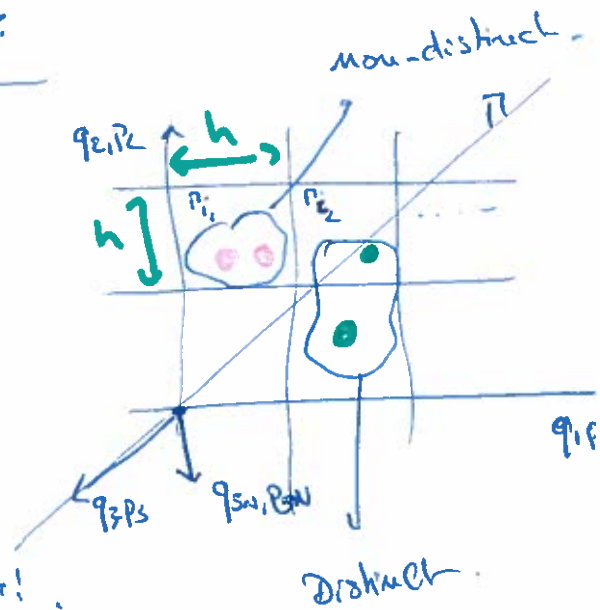
L2

• Gas of distinguishable particles:

Distinguishable configurations are $\vec{z} = (q, p)$ and $\vec{z}' = (q', p')$ that do not belong to the same Γ -cells.

or in other words:

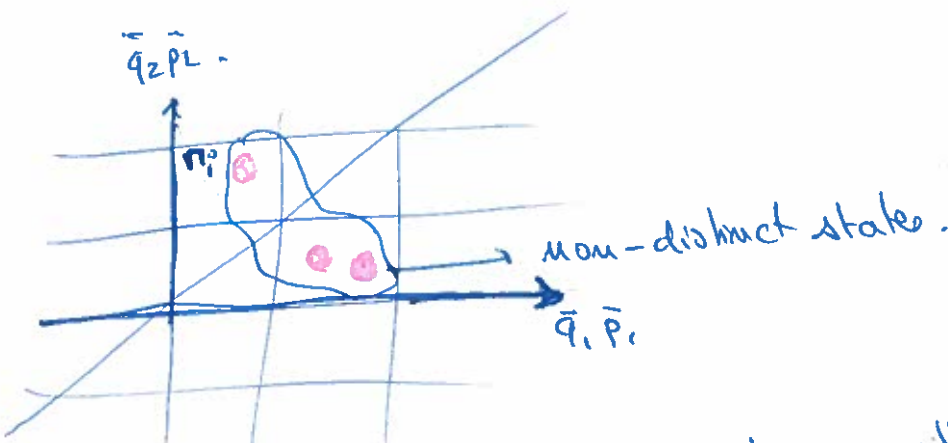
$\vec{z} \equiv \vec{z}'$ iff $\exists i, z \in \Gamma_i, z' \in \Gamma_i$.



• Gas of non-distinguishable particles:

$\vec{z} \equiv \vec{z}'$ iff $\exists i \in \mathbb{N}, \exists \sigma \in S_N$ permutation $z_\sigma \in \Gamma_i, z' \in \Gamma_i$

where $z_\sigma \equiv (q_{\sigma(1)} \bar{p}_{\sigma(1)}, q_{\sigma(2)} \bar{p}_{\sigma(2)}, \dots, q_{\sigma(N)} \bar{p}_{\sigma(N)}) \in \mathbb{R}^3$



In practice, we will deal with gas of non-distinguishable particles (but likely composed of \neq species!)

Thermodynamic observables:

A set of functions $X_1, \dots, X_m: \mathbb{R}^{2n} \rightarrow \mathbb{R}$.

Specifying the macroscopic properties of the system.

obs: in principle, the X_i 's should be constant over a Γ -cell.

Thermodynamic state:

A set of values for the observables.

Equilibrium:

Average values for the thermodynamic state in the limit $t \rightarrow \infty$

Either
$$\bar{X} = \lim_{t \rightarrow \infty} \int_0^t X(q(s), p(s)) ds.$$

or
$$\langle X \rangle = \lim_{t \rightarrow \infty} \lim_{\Omega \rightarrow \infty} \frac{1}{\Omega} \sum_{\omega=1}^{\Omega} X [q(t, \omega), p(t, \omega)]$$

$$\downarrow$$

experimental.

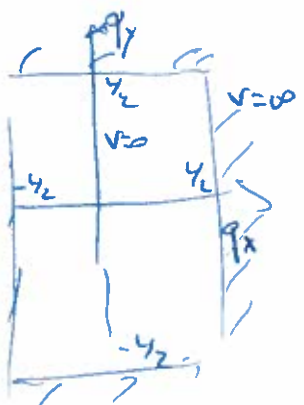
These values prescribe an equilibrium distribution f_{eq}

such that
$$\left[\begin{aligned} \langle X \rangle = \bar{X} &= \int f_{eq}(p, q) d\bar{p}d\bar{q} \\ 1 &= \int f_{eq}(p, q) d\bar{p}d\bar{q} \end{aligned} \right.$$

• To describe physical gas, (such as air) the most simple but relevant model is that of a gas composed of non-distinguishable particles.

• In practice, gas are made of several types of atoms/molecules, A more relevant model is to assume that the N particles are distributed among p different species, with $N_i = \#$ particles of species i . The natural physical assumption is then that particles of the same species are non-distinguishable.

• The most simple Hamiltonian in that context is that of a perfect gas: $H_N = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + V[\vec{q};] + \text{const}$



$$V(\vec{q}) = 0 \quad \text{if } \vec{q} \in \mathcal{Q}$$

$$= \infty \quad \text{otherwise}$$

• $\neq m_i$ represent \neq types of particles.

Ex: Air at room temperature:
 Oxygen: 20%
 Argon \approx 1%
 Nitrogen \approx 78%

Others: CO₂ (0.03%)
 Neon
 Helium } (< 1%)

$\rho_{\text{air}} = 22 \text{ g/mol}$ \approx 1g has $\approx 10^{21}$ molecules
 ($\approx 1 \text{ dm}^3 = 1 \text{ L}$)

② Entropy and second law: Gibbs equilibrium!

15

The Gibbs entropy of a physical gas (not necessarily at equilibrium)

$$S_G[\rho] = - \int_{\mathbb{R}^{2N}} d\vec{p} d\vec{q} \rho \log(\rho h^N)$$

[Distinguishable case]

$$= - \int \rho \log(\rho h^N N_1! N_2! \dots N_p!)$$

[p distinguishable species of non-distinguishable parts]

Obs: ρ is defined in terms of an "ensemble" as integration over a finite time window of a single experiment.

Two cases are in fact one: the limiting case of ...

N different species yields $S_G[\rho] = - \int \rho \log \rho h^N (1 \dots 1) = - \int \rho \log \rho h^N$

(This is Alexei's formula, dating from first week).

the case of a single species of which is:

$$S_G[\rho] = - \int \rho \log \rho h^N N!$$

S_G is defined in terms of a ∇ -space integration:

$$\int \rho d\vec{p} d\vec{q} = 1$$

in this definition S_G has no unit, or rather it is expressed in a unit of (k_B) .

Propy (Additivity):

$$\text{if } \rho = \rho(\vec{p}_1, \vec{q}_1) \rho(\vec{p}_2, \vec{q}_2) \quad \text{then:}$$

\uparrow first species \uparrow second species

$$S_G[\rho] = S_G[\rho_1] + S_G[\rho_2]$$

The Gibbs entropy formula can be conveniently invoked to describe the equilibrium state as one of maximal entropy, through the

2nd law:

$$\begin{aligned}
 \text{(*)} \quad & \rho_{\text{eq}} \text{ solves: } S_G[\rho] \rightarrow \text{sup} & \langle 1 \rangle_{\rho} &= \int \rho \, d\mu = 1 \\
 & & \langle X_i \rangle_{\rho} &= X_i \quad \forall i \in \{1, \dots, M\}
 \end{aligned}$$

Solutions of (*) prescribe the Gibbs distribution:

$$\rho_N(\vec{\beta}) = \frac{e^{-\sum_{i=1}^M \beta_i X_i}}{h^{3N} N_1! \dots N_p! Z_G}$$

with: $-\partial_{\beta_i} \log Z_G = X_i$, $Z_G = \int d\mu \frac{e^{-\beta X_i(\mu)}}{h^{3N} N_1! \dots N_p!}$

Obs: • If the X_i 's are dynamical invariants, ρ_N solves the stationary Liouville eq: $\rho_N, H_N \in \mathcal{O}$.
 (All is well) - It is indeed an invariant measure.

• Equilibrium entropy:

$$\begin{aligned}
 S_G(\vec{\beta}) &= - \langle \log h^{3N} N_1! \dots N_p! \rangle = - \langle \log h^{3N} N_1! \dots N_p! - \beta_i X_i - \log Z_G \rangle \\
 &= \beta \cdot \langle X \rangle + \log Z_G
 \end{aligned}$$

$$S_G(\vec{\beta}) = \beta_0 \left[\beta \cdot \langle X \rangle - \frac{F}{\beta_0} \right]$$

$$\beta_0 F = - \log Z_G$$

Particular case: $m=1, p=1$ (Isolated Z of non-distinguishable particles) L7

2nd law:

$$S_a [g] \rightarrow \text{sup} \quad \langle 1 \rangle_g = 1 ; \langle H \rangle_g = \bar{E}$$

Gibbs: $P_B = \frac{1}{N! h^{3N}} e^{-\beta H} = \frac{1}{N! h^{3N}} e^{-\beta(H-F)}$ | $\partial_{\beta} \ln Z_N = -E$
 $Z_N = \int \frac{e^{-\beta H}}{N! h^{3N}}$

Entropy: $S_P = \beta \left[\langle H \rangle - F \right]$
↑
Free energy.

$\beta = \frac{1}{T} \Rightarrow$ Inverse Temperature. (Obs: units of $h^3 \beta$ is an inverse energy!)

Example: Perfect gas: $H_N = \sum_{i=1}^N \frac{p_i^2}{2m} + V_i(q_i)$
 $Z_N = \frac{V^N}{N! h^{3N}} \left(\frac{2m\pi}{\beta} \right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$

(we put units back)

$$\lambda = \frac{h}{\sqrt{2m\pi k_B T}}$$

$$\left[\begin{aligned} E &= \frac{3}{2} N k_B T \\ F &= -k_B T N \left[\log \frac{V}{N \lambda^3} + 1 \right] \\ S &= N k_B T \left[\log \frac{V}{N \lambda^3} + \frac{5}{2} \right] \end{aligned} \right.$$

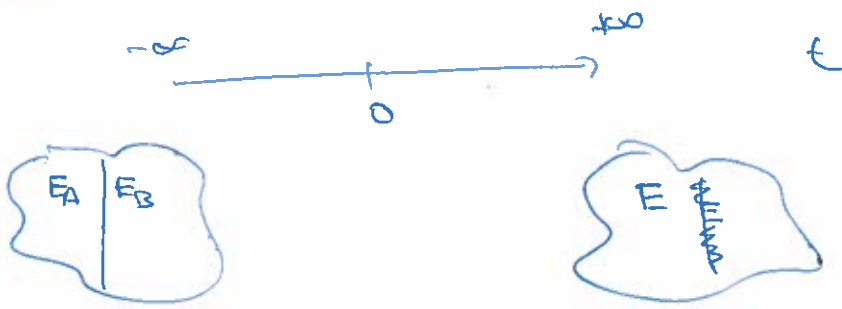
$$P_D = \left(\frac{\beta}{2m\pi} \right)^{3/2} \frac{1}{V^N} e^{-\beta \frac{\vec{p}^2}{2m}} \quad \text{1 per.}$$

\Rightarrow The distribution of velocity is gaussian and its variance is set by the temperature!

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \frac{1}{2\beta} = \frac{k_B T}{2}$$

Gibbs 2nd law and time arrow

- Gedanken experiment: transition between two equilibrium.



$$S^{(G)} = \text{Argmax} \left\{ S_G; \begin{matrix} E = H_A + H_B \\ E_A = H_A \\ E_B = H_B \end{matrix} \right\} \quad \ll \quad S^{(P)} = \text{Argmax} \left\{ S_G; E = H_A + H_B \right\}$$

- Removing constraints "mechanically" increase equilibrium entropy.
- "mix" / homogenize Lagrange multipliers.
($\beta_A, \beta_B \rightarrow \beta$).

- If $T_A \neq T_B$, Gibbs set clear time arrow. 2nd law allows the direction but not the reverse \leftarrow :
The system cannot come back to its initial state of equilibrium.

- This behavior is consistent with 19th century statement of irreversibility.
Energy flows from hot to cold, and not the other way around!
bath

Pb: • Gibbs entropy = "ensemble point of view"

- \Rightarrow How relevant for single system? $C \rightarrow$ "Eno equivalence"
- Contradicts micro dynamics?

if $z(t|z_0)$ is altered the time reversed

trajectory $\tilde{z}(-t | z(t|z_0))$ should be as well!

($t \rightarrow -t ; p \rightarrow -p$)

③ Boltzmann Entropy

L9

For a prescribed observational state, the Boltzmann entropy is:

$$S_0[X] = k_B \log W$$

distinct configurations $(p, q) \in R^m$
such that $\chi(\bar{p}, \bar{q}) = X$.

Obs: • Boltzmann entropy associates a value to each state, apparently independently of the distribution.
• Applies to single system. (unlike Gibbs)

Second Law [Boltzmann]:

- Macrostates of higher entropy are realized by an overwhelming number of microstates.
- The equilibrium values of the states are prescribed by those of high entropy.

In other words: Typical states are the averaged state.

Link between Gibbs and Boltzmann Entropy at Equilibrium

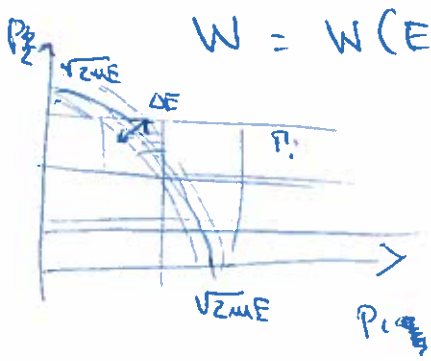
- Under suitable conditions they match! (at equilibrium)
- (But sometimes they don't!)

Example: Perfect gas (again!) in the case $\underline{m=1, p=1}$

One identifies the number of distinct configurations with

$$W = W(E, V, N) = \frac{1}{N!} \frac{V^N A_{3N}^{(R_E)}(\Delta E)}{h^{3N}} \quad R_E = \sqrt{2mE}$$

$$= \frac{V^N}{N! h^{3N}} \Delta E \left[\frac{2\pi^{\frac{m+1}{2}} R_E^m}{\Gamma(\frac{m+1}{2})} \right] \quad m=3N$$



↳ area of the m -sphere of radii

Using Stirling's formula, one omits immediately:

$$\frac{S_B}{k_B} = \log W = N \left[\log \frac{V}{h^3 N} + 1 \right] + \frac{3N}{2} \left[\log \left[\frac{2\pi}{h^2} \frac{2mE}{3N} \right] + 1 \right]$$

$$+ \log \Delta E \quad (\text{const})$$

$$= N \log \left[\frac{V}{h^3 N} + \frac{E}{2} \right] \quad \text{with } \lambda_E = \frac{h}{(2mE\pi/3N)^{1/2}}$$

Upon defining

$$\frac{1}{T} \stackrel{!}{=} \frac{\partial}{\partial E} S_B = \frac{3N}{2E} k_B \Rightarrow E = \frac{3}{2} N k_B T \quad \text{and } \underline{\lambda_E = \lambda_E}$$

(previously defined)

Obs / S is extensive, E is extensive

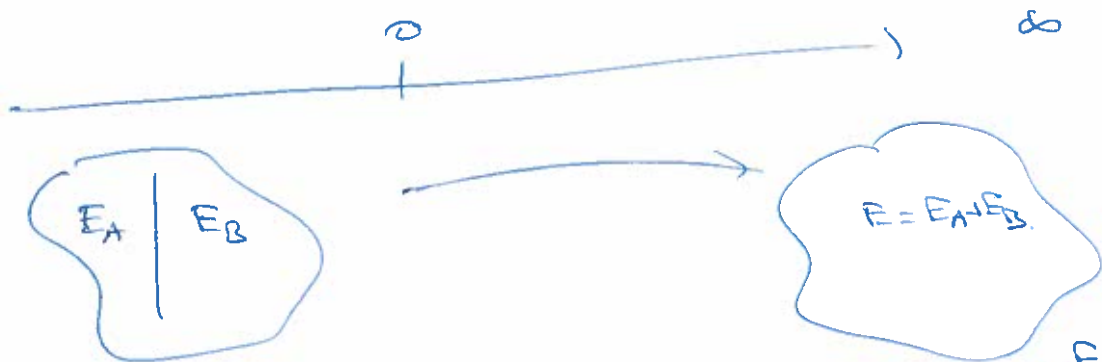
$$S = S(E, V, N) = N S\left(\frac{E}{N}, \frac{V}{N}, 1\right)$$

Obs. $S_B = S_A(\text{seq})$ for the perfect gas, especially!

This result is in fact more general and relates to equivalence of statistical ensemble valid for a large class of systems, ^(A) with short-range interactions.

(cf Appendix)

Obs. Second law à Boltzmann sets a preferred arrow of time, without ruling out improbable events:



$$W^{(G)} = W_A(E_A^0) W_B(E_B^0) \Delta E$$

$$W^{(CP)} = \int_{E_A^0}^E W_A(E_A) W_B(E - E_A) dE_A \\ \geq W_A(E_A^0) W_B(E_B^0)$$

$$\Rightarrow \boxed{S_B^{(CP)} - S_B^{(G)} \geq 0}$$

Here the entropy difference explains the behaviour of the typical microstate, without contradiction (in appearance!) with microscopic dynamics.

(4) Paradoxical mixing 1:

Should perfect gas spontaneously expand?

Thermic: $\Delta S = N k_B \log 2 > 0$

Yes! \rightarrow

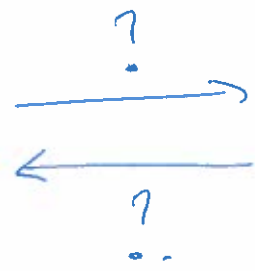
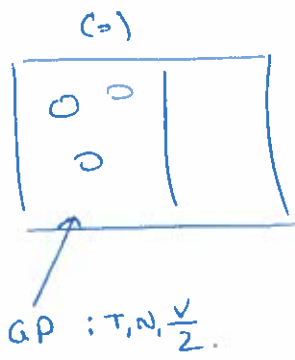
Microscopic: Not necessarily.

Hamilton's mechanics is symmetric
 $t \rightarrow -t$.

Hence if \rightarrow is allowed, so

is \leftarrow .

\Rightarrow No preferred time arrow!



$$S^{(a)} = N k_B \log \left(\frac{V}{2N} \right) + \frac{S}{2}$$

$$S^{(b)} = N k_B \log \left(\frac{V}{N} \right)$$

Q: Is microscopic reversibility in contradiction with the second law?

Answer: No, not necessarily. The apparent paradox is resolved with Boltzmann's view, by the word overwhelming and the disjunct microstate/macrostate

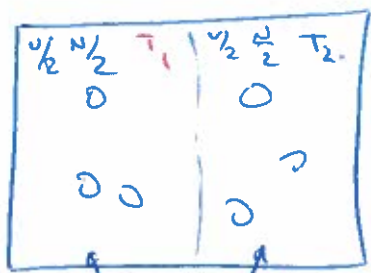
For 1g of air $\Delta S \sim (k_B \log 2) 10^{23}$

$$\frac{W^{(b)}}{W^{(a)}} = e^{\Delta S/k_B} \sim 2^{10^{23}}$$

with the interpretation of equilibrium state as a time-average over trajectories, this implies that the typical time between two anomalous states (Φ) is $2^{10^{23}}$, a number so huge that it is the same whether it is expressed in terms of seconds or age of the universe ($\sim 10^{10}$ years)

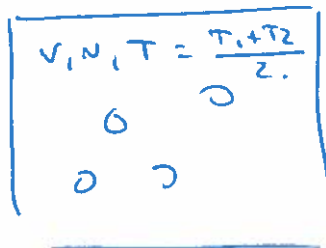
Paradoxical mixing 2:

Should perfect gas thermalize?



same perfect gas

Thermo \rightarrow



Thermo:

$$S^{(G)} = N k_B \left[\frac{5}{2} + \frac{1}{2} \log \frac{V/2^2}{N/2^2 \lambda^3} \frac{V/2}{N/2^2} \right]$$

$$S^{(H)} = N k_B \left[\frac{5}{2} + \log \frac{V}{N \lambda^3} \right]$$

$$\Delta S = \frac{3}{2} N k_B \log \frac{T}{\sqrt{T_1 T_2}}$$

concavity
(Ex: check!)

Hamiltonian: No preferred direction of time, microscopic configuration will be ultimately recovered.
(Same as previously).

Boltzmann: - Reversibility argument irrelevant.
For $T_1 \sim 293K, T_2 \sim 301K$ $e^{\Delta S/k_B} \sim e^{10^{17}}$ [still - very very big]
• But more importantly there is no interaction between the molecules if the gas are perfect [Perfect gas do not 'collide'].
 \Rightarrow No thermalization possible!!

(cf slides)

② • This argument of Boltzmann in fact implies that (*) is not correct. why? [cf. Jaynes' paper: Gibbs paradox]

• How to reconcile classical mechanics and thermo?
This involves dealing with interactions. This is the subject of the lecture to come!

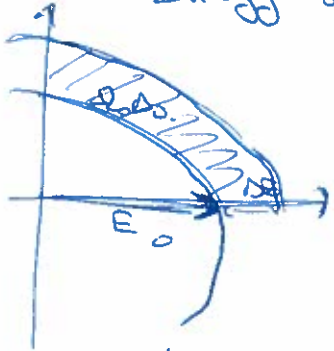
Add-on:

14

⑤ Two ways to correlate between Gibbs and Boltzmann.

① Boltzmann Formula can be obtained from Gibbs entropy applied to the uniform distribution over the

Energy surface E . or rather: $\rho(E) = \frac{1}{\Omega(E)\Delta E_0} \mathbb{1}_{E \in [E_0, E_0 + \Delta E_0]}$



with $\Omega(E_0) = \frac{d}{dE_0} \int dp dq \mathbb{1}_{H(p,q) \leq E_0}$

$$S_G[\rho] = - \int \rho \log \rho h^{3N} \pi^{3N} dp dq.$$

$$= - \int dE \rho(E) \log \rho h^{3N} (\pi^{3N}) \times \Omega(E).$$

$$= \int_{E \in [E_0, E_0 + \Delta E_0]} \frac{\Omega(E) dE}{\Omega(E_0) \Delta E_0} \left(\log \frac{h^{3N} (\pi^{3N})!}{\Omega(E_0) \Delta E_0} \right)$$

$\hookrightarrow = - S_B(E_0).$

$$\Rightarrow \boxed{S_G(\rho) = S_B(E_0)}$$

② Under a certain number of assumptions, such as:

$$S_B(E, N) \sim N S_B\left(\frac{E}{N}, \Delta\right) \quad (\text{Extensivity})$$

$$E_N \sim N E \quad (\text{Extensivity})$$

$N \rightarrow \infty$

$$\frac{d}{dE^2} S_B(E, N) < 0 \quad (\text{Concavity})$$

$$S_B = S_G[\rho_B]$$

↑
Gibbs distribution

2/ general argument relies on a steepest descent argument.

Gibbs: $P_F = \frac{1}{\pi N!} \frac{1}{h^{3N}} e^{-\beta H}$ $E_N = -\partial_\beta \log Z_N$

$$\Rightarrow e^{-\beta F} = Z_N = \frac{1}{h^{3N}} \frac{1}{\pi N!} \int e^{-\beta H} dp dq$$

$$= \int dE \left[\frac{\Omega(E)}{h^{3N} (\pi N!)} \right] e^{-\beta E}$$

$$\approx \int d(E) e^{N S_B \left[\frac{E_N}{N} \right] - \beta N \left(\frac{E_N}{N} \right)}$$

$$\approx N \int d\epsilon e^{N(S_B(\epsilon) - \beta \epsilon)}$$

$$\Rightarrow -\beta F \approx N(S_B(\epsilon^*) - \beta \epsilon^*) \quad \text{with } \epsilon^* = \text{argmax}(S_B(\epsilon) - \beta \epsilon)$$

This implies

- $F_N(\beta) \underset{N \rightarrow \infty}{\approx} E_N^* - \beta^{-1} S_B[E_N^*, N]$

- $E_N^* = \partial_\beta \beta F = \langle H \rangle_\beta = E \quad (N \rightarrow \infty)$

- $S_a[\beta] = \beta [\langle H \rangle_\beta - \beta F]$
 $\approx \beta [E - E + \frac{1}{\beta} S_B(E_N^*, N)]$

$$S_a(\beta) \approx S_B(E_N^*, N)$$

