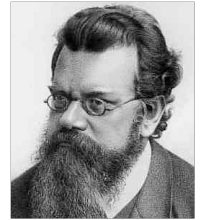


04. Entropy in Statistical Mechanics

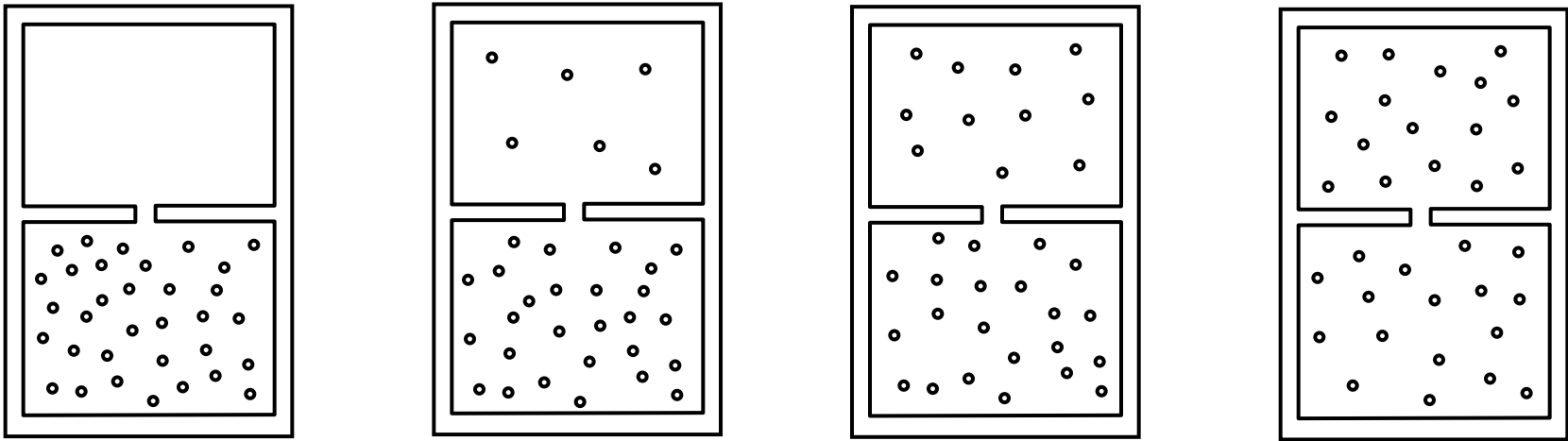
- Goal: To explain the behavior of *macroscopic* systems in terms of the dynamical laws governing their *microscopic* constituents.
 - In particular: To provide a *micro-dynamical* explanation of the 2nd Law.



Ludwig Boltzmann
(1844-1906)

1. Boltzmann's Approach to Statistical Mechanics

- Consider different "macrostates" of a gas at constant energy:



- Why does the gas prefer to be in the equilibrium macrostate (last one)?

Thermodynamic equilibrium macrostate = state characterized by thermodynamic properties (temp, volume, pressure, etc.) that do not change with time.

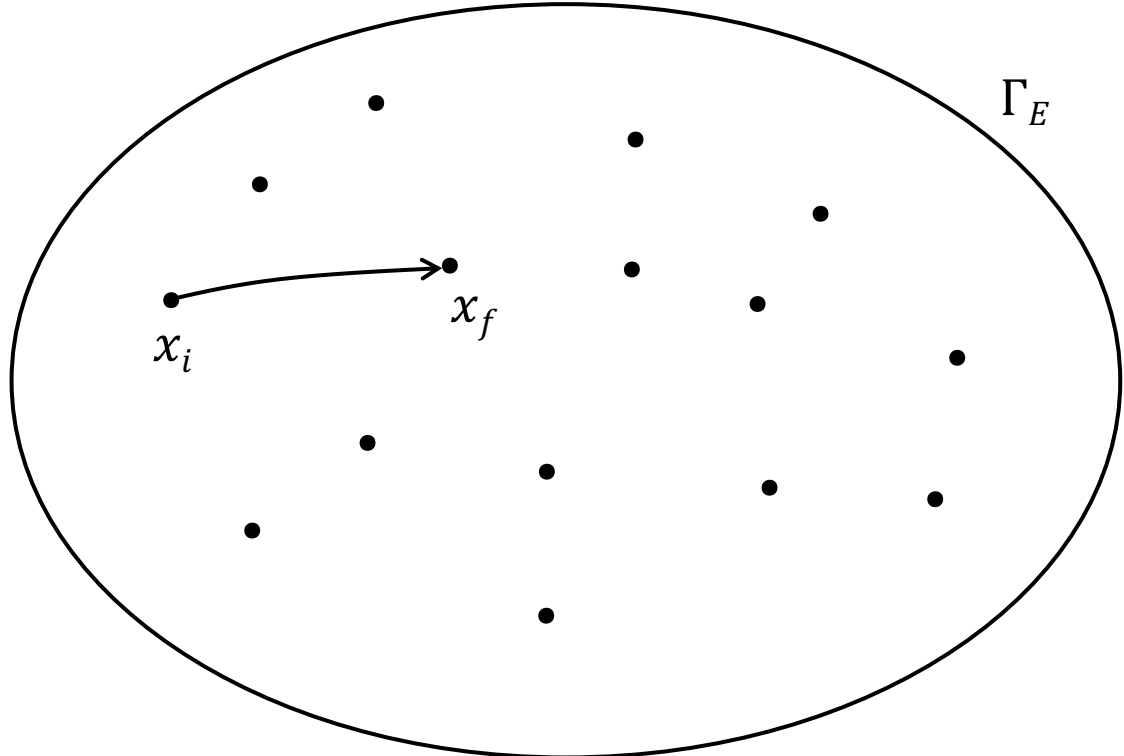
- Suppose the gas consists of N particles governed by Hamilton's equations of motion (the micro-dynamics).

Def. 1 (*Microstate*). A **microstate** x of an N -particle system is a specification of the position (3 values) and momentum (3 values) for each of its N particles.

Let $\Gamma = \textit{phase space} = 6N\text{-dim space of all possible microstates.}$

Let $\Gamma_E = \textit{region of } \Gamma \textit{ that consists of all microstates with constant energy } E.$

Hamiltonian dynamics maps initial microstate x_i to final microstate x_f .



Can 2nd Law be explained in terms of this dynamics?

Def. 2 (Macrostate). A **macrostate** Γ_M of a physical system is a specification of the system in terms of macroscopic properties (pressure, temperature, volume, *etc.*).

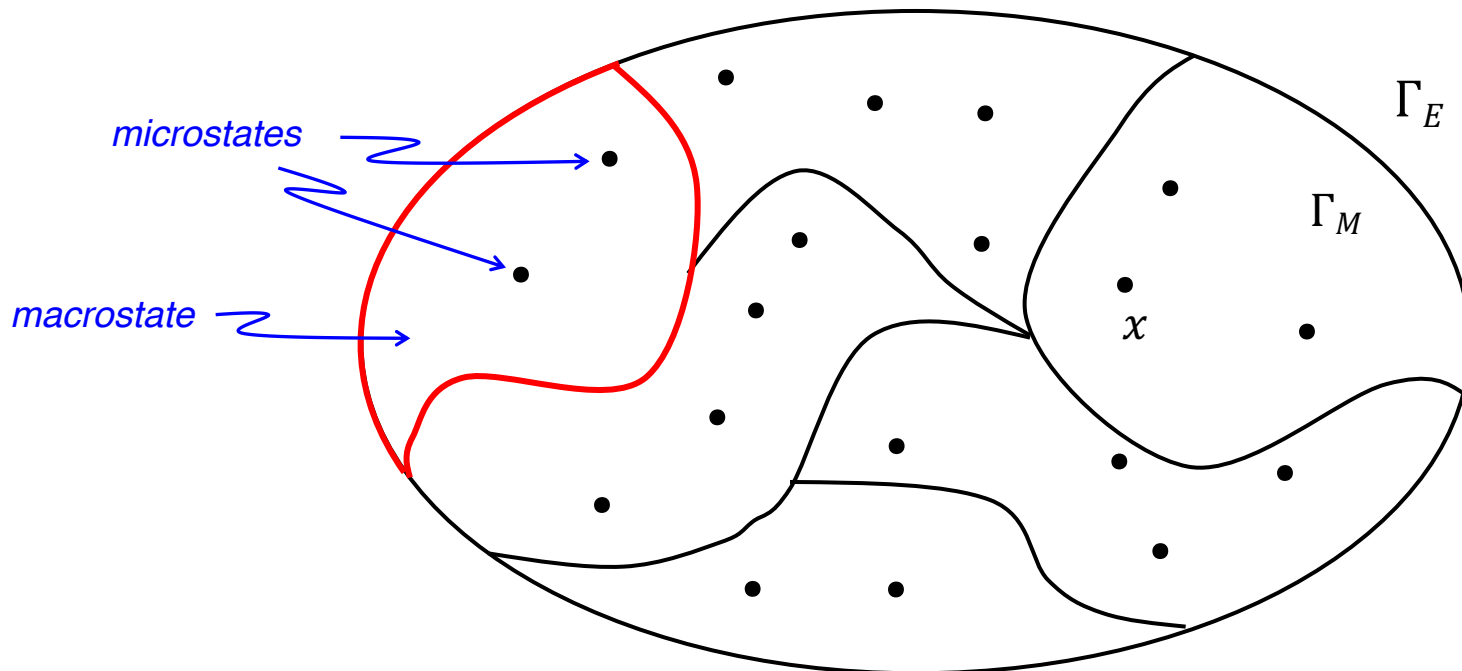
- Relation between microstates and macrostates:



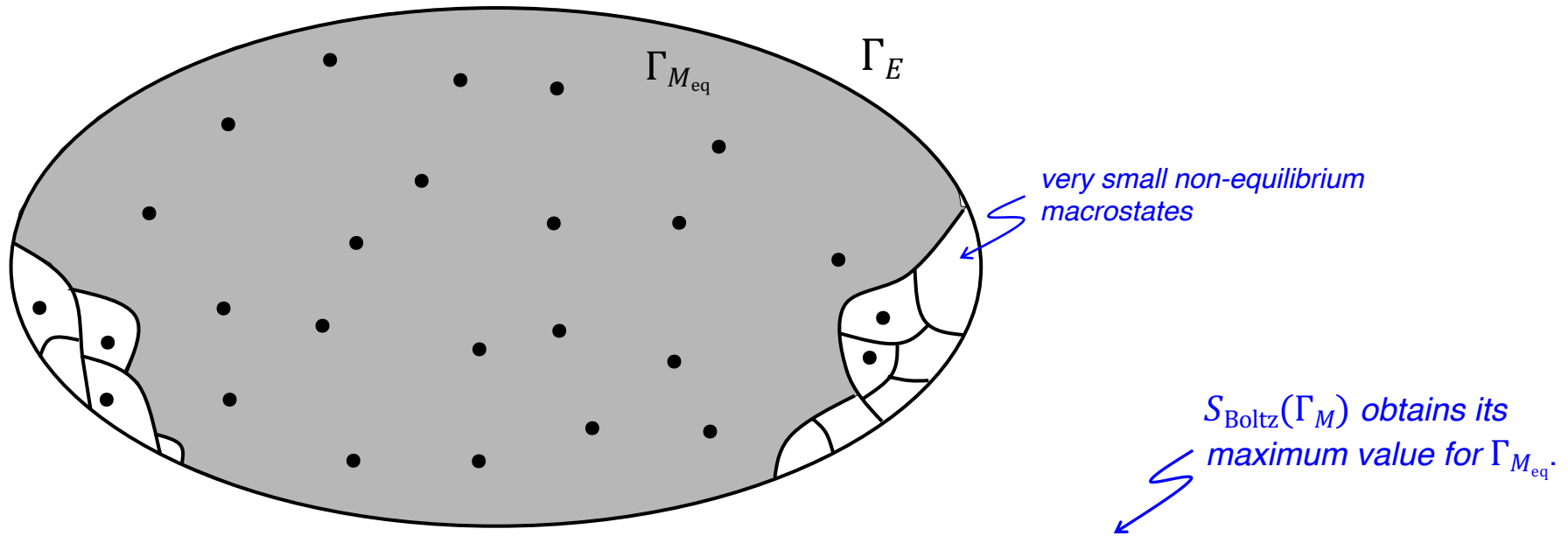
Macrostates supervene
on microstates!

- To each microstate there corresponds exactly one macrostate.
- Many distinct microstates can correspond to the same macrostate.

- So: Γ_E is partitioned into a finite number of regions Γ_M corresponding to macrostates, with each microstate x belonging to one macrostate.



Assumption. The equilibrium macrostate $\Gamma_{M_{eq}}$ is *much larger* than any other macrostate.



Def. 3 (Boltzmann entropy). The **Boltzmann entropy** $S_{Boltz}(\Gamma_M)$ of a macrostate Γ_M of an isolated physical system at constant energy is given by $S_{Boltz}(\Gamma_M) \equiv k \ln |\Gamma_M|$, where $|\Gamma_M|$ is the size of Γ_M .

Claim. S_{Boltz} increases over time because, for any initial microstate x_i , the dynamics will map x_i into $\Gamma_{M_{eq}}$ very quickly, and then keep it there for an extremely long time.

But why?

Two Ways to Explain the Approach to Equilibrium:

(a) Appeal to Typicality Goldstein (2001)

Claim. A system approaches equilibrium because equilibrium microstates are *typical* and nonequilibrium microstates are *atypical*.

- Why? For large N , Γ_E is almost entirely filled up with equilibrium microstates. Hence they are "typical".

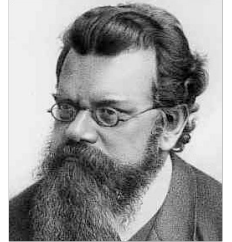
- But: What is it about the *dynamics* that evolves atypical states to typical states?
 - "If a system is in an atypical microstate, it does not evolve into an equilibrium microstate *just because* the latter is typical." (Frigg 2009)
 - Need to identify properties of the dynamics that guarantee atypical states evolve into typical states.
 - And: Need to show that these properties are typical.
 - Ex: If the dynamics is *chaotic* (in an appropriate "ergodic" sense), then (under certain conditions), any initial microstate x_i will quickly be mapped into Γ_{eq} and remain there for long periods of time. (Frigg 2009)

(b) Appeal to Probabilities

Claim. A system approaches equilibrium because it evolves from states of lower toward states of higher probability, and the equilibrium state is the state of highest probability.

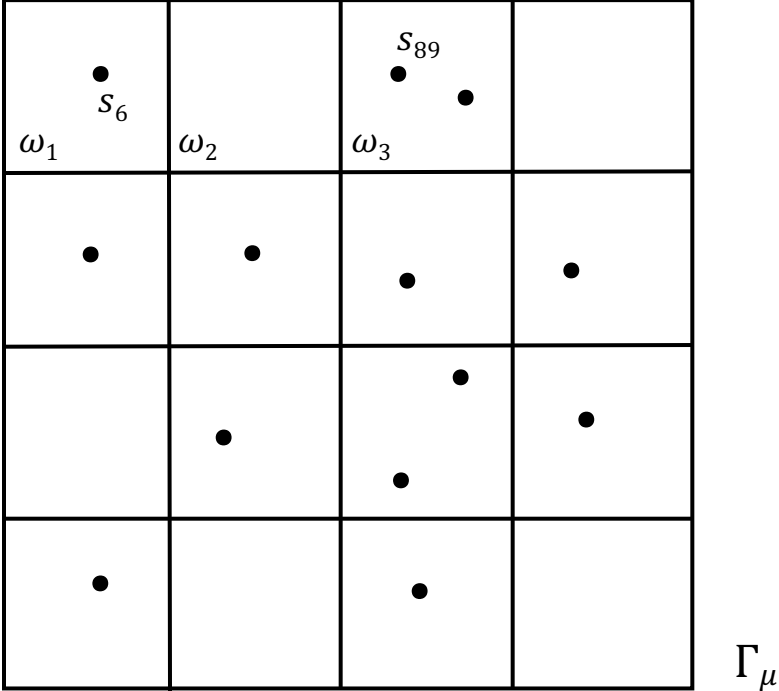
- Associate probabilities with macrostates: the larger the macrostate, the greater the probability of finding a microstate in it.

"In most cases, the initial state will be a very unlikely state. From this state the system will steadily evolve towards more likely states until it has finally reached the most likely state, i.e., the state of thermal equilibrium."



Task: *Make this a bit more precise (Boltzmann's combinatorial argument)...*

Coarse-graining the single-particle phase space



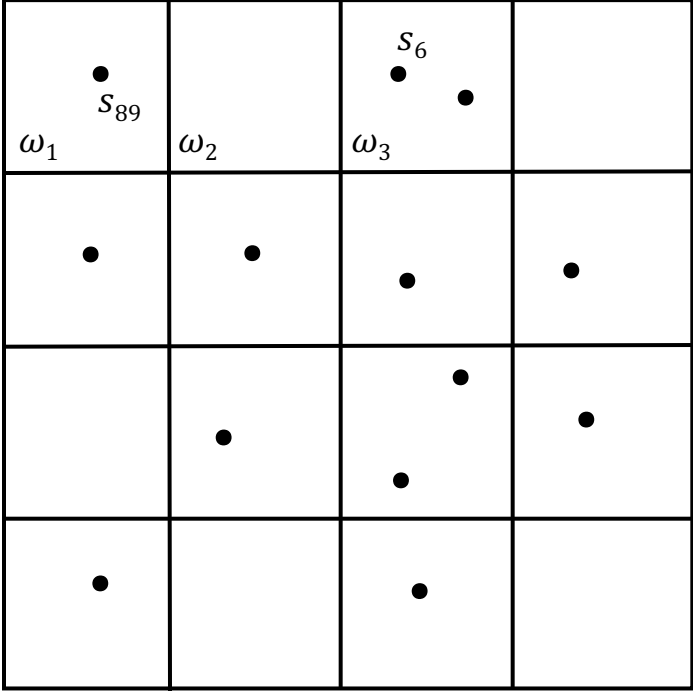
Arrangement #1:
state s_6 in ω_1 , state s_{89} in ω_3 , etc.

- Start with the 6-dim phase space Γ_μ of a single particle.
- Partition Γ_μ into ℓ cells $\omega_1, \dots, \omega_\ell$ of size $\delta\omega$.
- A state of an N -particle system is given by N points in Γ_μ .

← *- A point in Γ_μ is a single-particle microstate.*
- $\Gamma_E = N$ copies of Γ_μ

Def. 4. An **arrangement** is a specification of *which* states lie in which cells.

Coarse-graining the single-particle phase space



Arrangement #1:
state s_6 in ω_1 , state s_{89} in ω_3 , etc.

Arrangement #2:
state s_{89} in ω_1 , state s_6 in ω_3 , etc.

Distribution:
 $D = (1, 0, 2, 0, 1, 1, \dots)$

1 state in ω_1 , 0 states in ω_2 , 2 states in ω_3 , etc.

- Start with the 6-dim phase space Γ_μ of a single particle.
- Partition Γ_μ into ℓ cells $\omega_1, \dots, \omega_\ell$ of size $\delta\omega$.
- A state of an N -particle system is given by N points in Γ_μ .

- A point in Γ_μ is a single-particle microstate.
- $\Gamma_E = N$ copies of Γ_μ

Def. 4. An **arrangement** is a specification of *which* states lie in which cells.

Def. 5. A **distribution** $D = (n_1, n_2, \dots, n_\ell)$ is a specification of *how many* states (regardless of *which* ones) lie in each cell.

More than one arrangement can correspond to the same distribution!

How many arrangements $G(D)$ are compatible with a given $D = (n_1, n_2, \dots, n_\ell)$?

• Answer:

$$G(D) = \frac{N!}{n_1! n_2! \dots n_\ell!} = \left(\begin{array}{l} \text{Number of ways to arrange } N \\ \text{distinguishable objects into } \ell \\ \text{bins with capacities } n_1, n_2, \dots, n_\ell. \end{array} \right)$$

$n! = n(n-1)(n-2)\dots 1$
 $= \# \text{ of ways to arrange } n \text{ distinguishable objects}$
 $0! = 1$

Check: Let $D_1 = (N, 0, \dots, 0)$ and $D_2 = (N-1, 1, 0, \dots, 0)$.

$$G(D_1) = \frac{N!}{N!} = 1 \quad \leftarrow \text{Only one way for all } N \text{ particle states to be in } w_1.$$

$$G(D_2) = \frac{N!}{(N-1)!} = \frac{N(N-1)(N-2)\dots 1}{(N-1)(N-2)\dots 1} = N \quad \leftarrow \text{There are } N \text{ different ways } w_2 \text{ could have one state in it; namely, if } s_1 \text{ was in it, or if } s_2 \text{ was in it, or if } s_3 \text{ was in it, etc..}$$

How many arrangements $G(D)$ are compatible with a given $D = (n_1, n_2, \dots, n_\ell)$?

• Answer:

$$G(D) = \frac{N!}{n_1! n_2! \dots n_\ell!} = \left(\begin{array}{l} \text{Number of ways to arrange } N \\ \text{distinguishable objects into } \ell \\ \text{bins with capacities } n_1, n_2, \dots, n_\ell. \end{array} \right)$$

$n! = n(n-1)(n-2)\dots 1$
 $= \# \text{ of ways to arrange } n \text{ distinguishable objects}$
 $0! = 1$

Assumption 1. The probability of a distribution D is given by $G(D)$.

"The probability of this distribution [D] is then given by the number of permutations of which the elements of this distribution are capable, that is by the number [$G(D)$]. As the most probable distribution, i.e., as the one corresponding to thermal equilibrium, we again regard that distribution for which this expression is maximal..."



In other words:

Claim. The equilibrium distribution is the distribution that maximizes $G(D)$.

Next task: What form does this distribution take?

Assumption 2. Each distribution D corresponds to a macrostate Γ_{M_D} .

Why? A system's macroscopic properties (volume, pressure, temp, etc) only depend on how many particles are in particular microstates, and not on which particles are in which microstates.

What is the size of this macrostate?

- A point in (the big phase space) Γ_E corresponds to an arrangement in (the single-particle phase space) Γ_μ .
- The size of a macrostate Γ_{M_D} in Γ_E is given by the number of points it contains (the number of arrangements compatible with D) multiplied by a *volume element* of Γ_E .
- A volume element of Γ_E is given by N copies of a volume element $\delta\omega$ of Γ_μ .

• So: The size of Γ_{M_D} is $|\Gamma_{M_D}| = \left[\begin{array}{l} \# \text{ arrangements} \\ \text{compatible with } D \end{array} \right] \times \left[\begin{array}{l} \text{volume} \\ \text{element of } \Gamma_E \end{array} \right]$

$$= G(D)\delta\omega^N$$

The probability $G(D)$ of D is proportional to the size of Γ_{M_D}

• Hence: $S_{\text{Boltz}}(\Gamma_{M_D}) = k \ln(G(D)\delta\omega^N)$

$$= k \ln(G(D)) + Nk \ln(\delta\omega)$$

$$= k \ln(G(D)) + \text{const.}$$

S_{Boltz} as a measure of how probable a macrostate is.

Other formulations of S_{Boltz} :

$$S_{\text{Boltz}}(\Gamma_{M_D}) = k \ln(G(D)) + \text{const.}$$

$$= k \ln\left(\frac{N!}{n_1! \cdots n_\ell!}\right) + \text{const.}$$

Stirling's approx:
 $\ln n! \approx n \ln n - n$

$$n_1 + \cdots + n_\ell = N$$

$$= k \ln(N!) - k \ln(n_1!) - \cdots - k \ln(n_\ell!) + \text{const.}$$

$$\approx (Nk \ln N - N) - (n_1 k \ln n_1 - n_1) - \cdots - (n_\ell k \ln n_\ell - n_\ell) + \text{const.}$$

$$= -k \sum_{i=1}^{\ell} n_i \ln n_i + \text{const.}$$

S_{Boltz} in terms of single-particle microstate occupation numbers n_i .

• Let: $p_i = n_i/N = \left[\begin{array}{l} \text{probability of finding a} \\ \text{randomly chosen single-} \\ \text{particle microstate in cell } \omega_i \end{array} \right]$

Probabilities for single-particle micro-states (not macrostates or distributions)!

• Then: $S_{\text{Boltz}}(\Gamma_{M_D}) = -Nk \sum_{i=1}^{\ell} p_i \ln p_i + \text{const.}$

S_{Boltz} in terms of single-particle microstate probabilities p_i .

• Or: $S_{\text{Boltz}}(\Gamma_{M_D}) = -Nk \int_{\Gamma_\mu} \rho_\mu(x_\mu) \ln \rho_\mu(x_\mu) dx_\mu$

probability distribution over Γ_μ

What distribution $D^* = (n_1^*, \dots, n_\ell^*)$ maximizes $S_{\text{Boltz}}(n_i)$?

Assume: The n_i are constrained by
 (a) $\sum_{i=1}^{\ell} n_i = N$ (b) $\sum_{i=1}^{\ell} \varepsilon_i n_i = U$

*Weak interaction assumption:
 The total internal energy $U =$ sum of the energies ε_i of each particle*

- To maximize $S_{\text{Boltz}}(n_i)$, set its derivative to zero and solve for n_i :

$$(d/dn_i)S_{\text{Boltz}}(n_i) = -k \sum_i (d/dn_i)(n_i \ln n_i + \text{const.}) = -k \sum_i (\ln n_i + 1)$$

- Or: $dS_{\text{Boltz}} = -k \sum_i (\ln n_i + 1) dn_i$ *Small changes to S_{Boltz} due only to small changes dn_i*

- Now find values n_i^* that solve:

$$dS_{\text{Boltz}} = -k \sum_i (\ln n_i^* + 1) dn_i = 0$$

subject to constraints $\begin{cases} dN = \sum_i dn_i = 0 \\ dU = \sum_i \varepsilon_i dn_i = 0 \end{cases}$

- Can add arbitrary multiples of the constraints and still get zero:

$$dS_{\text{Boltz}} = \sum_i (-k \ln n_i^* - \alpha - \beta \varepsilon_i) dn_i = 0$$

So: $k \ln n_i^* + \alpha + \beta \varepsilon_i = 0$ or $n_i^* = e^{-(\alpha + \beta \varepsilon_i)/k} = e^{-\alpha/k} e^{-\beta \varepsilon_i/k}$

Now put this into a (slightly) nicer form...

What distribution $D^* = (n_1^*, \dots, n_\ell^*)$ maximizes $S_{\text{Boltz}}(n_i)$?

Assume: The n_i are constrained by
(a) $\sum_{i=1}^{\ell} n_i = N$ (b) $\sum_{i=1}^{\ell} \varepsilon_i n_i = U$

*Weak interaction assumption:
The total internal energy $U =$ sum
of the energies ε_i of each particle*

- Enforce (a) on $n_i^* = e^{-\alpha/k} e^{-\beta \varepsilon_i/k}$

$$\sum_i n_i^* = N = e^{-\alpha/k} \sum_i e^{-\beta \varepsilon_i/k} \quad \text{or} \quad e^{-\alpha/k} = N/Z, \quad Z \equiv \sum_i e^{-\beta \varepsilon_i/k}$$

- So: $n_i^* = (N/Z) e^{-\beta \varepsilon_i/k}$

- Hence:

$$D^* = (n_1^*, \dots, n_\ell^*) = \left(\frac{N}{Z} e^{-\beta \varepsilon_1/k}, \dots, \frac{N}{Z} e^{-\beta \varepsilon_\ell/k} \right)$$

← The "Maxwell-Boltzmann distribution"

Boltzmann's claim:
 D^* is the equilibrium distribution

How S_{Boltz} relates to S_{TD}

- Consider: Small changes in internal energy of a reversible process:

<u>Macroscopic point of view</u>	<u>Microscopic point of view</u>
$dU = \delta Q - dW$	$dU = d(\sum_i \varepsilon_i n_i)$
$= TdS_{\text{TD}} - PdV$	$= \sum_i \varepsilon_i dn_i + \sum_i n_i d\varepsilon_i$

- Intuitions:
 - A change in volume dV causes a change in energy $d\varepsilon_i$.
 - A change in entropy dS_{TD} is related to a change in microstate number dn_i .

- Suggests: $PdV = -\sum_i n_i d\varepsilon_i$ and $dS_{\text{TD}} = (1/T)\sum_i \varepsilon_i dn_i$

- Note: For the Max-Boltz equilibrium distribution $n_i^* = \frac{N}{Z} e^{-\beta \varepsilon_i/k}$:


$$\begin{aligned}
 dS_{\text{Boltz}}(n_i^*) &= -k \sum_i (\ln n_i^* + 1) dn_i = -k \sum_i \left\{ \ln \frac{N}{Z} + 1 - \beta \varepsilon_i/k \right\} dn_i \\
 &= \beta \sum_i \varepsilon_i dn_i
 \end{aligned}$$

↙ $(\ln \frac{N}{Z} + 1) \sum_i dn_i = 0$

- So: For the M-B equilibrium distribution, $S_{\text{Boltz}} = S_{\text{TD}}$, provided $\beta = 1/T$.

What this shows:

- For a *large number of weakly interacting* particles in an equilibrium state, it is *consistent* to identify the Boltzmann entropy S_{Boltz} with the thermodynamic entropy S_{TD} .
- But:
 - Assumes the Maxwell-Boltzmann distribution D^* that maximizes S_{Boltz} is the equilibrium distribution (i.e., just another way of assuming that the largest macrostate is the equilibrium macrostate).
 - S_{TD} measures absolute changes in heat per temperature of a reversible process; whereas S_{Boltz} measures the size of a macrostate.
 - For thermally isolated processes, S_{TD} absolutely increases or remains constant; whereas there is no absolute law that requires S_{Boltz} to increase or remain constant.


What about the dynamics of a system entails that it will evolve:

- *to the largest macrostate?*
- *to the most typical macrostate?*
- *to the most probable macrostate?*



Willard Gibbs
(1839-1903)

2. Gibbs' Approach.

Boltzmann: Analysis of a *single* multiparticle system.

- Point x in Γ_E : possible microstate of system.
- Function f on Γ_E : a property of the system in terms of its micro-properties (positions/momenta of its particles).
- Problem: Observed macro-properties (temp, pressure, volume, etc) are time averages of micro-properties.



Very difficult to calculate! (Must keep track of all positions and momenta of particles of the system over a given period of time!)

- Gibbs' Solution:

Replace

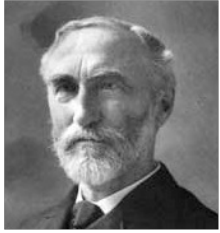
Time average of a property of a single system over a period of time.

with

"Ensemble average" of the property over infinitely many copies of the system at an instant of time!



Much easier to calculate! All you need is a weighting system defined on all the copies; i.e., a distribution $\rho(x)$ defined on Γ !



Willard Gibbs
(1839-1903)

2. Gibbs' Approach.

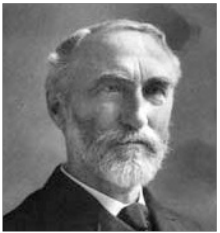
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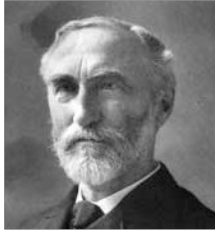
Gibbs: Analysis of an *ensemble* of infinitely many copies of same system.

- Point x in Γ : microstate of one member of ensemble.
- Function f on Γ : a property of the system in terms of its micro-properties.
- *Distribution* $\rho(x)$ on Γ : state of entire ensemble.

← Not Boltzmann's D
or $\rho_\mu(x_\mu)$!



"And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time."



Willard Gibbs
(1839-1903)

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- *Distribution* $\rho(x)$ on Γ : state of entire ensemble.

← Not Boltzmann's D or $\rho_\mu(x_\mu)$!

One way to think of difference

- *Boltzmann*: The state of a multiparticle system is represented by a point x in Γ_E .
- *Gibbs*: The state of a multiparticle system is represented by an ensemble $\{\Gamma, \rho(x)\}$, which is a collection Γ of possible states, with each state x weighted by a probability $\rho(x)$.

← Definite "pure" state?

← Indefinite "mixed" state?



Willard Gibbs
(1839-1903)

2. Gibbs' Approach.

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- *Distribution* $\rho(x)$ on Γ : state of entire ensemble.

← Not Boltzmann's D
or $\rho_\mu(x_\mu)$!

$$\int_S \rho(x) dx \quad \leftarrow \text{Probability of finding state of a system in region } S$$

$$\langle f \rangle \equiv \int_\Gamma f(x) \rho(x) dx \quad \leftarrow \text{Ensemble average of } f$$

- *Stationary distribution*: constant in time.
- Note: $\langle f \rangle$ is constant just when ρ is stationary.

← If macro-properties are represented by ensemble averages, then they don't change in time for stationary distributions.

Averaging Principle: The measured value of a property f of a system in thermodynamic equilibrium is the ensemble average $\langle f \rangle$ of an ensemble in statistical equilibrium (i.e., an ensemble with a stationary distribution).

Justification: A measurement of a property f takes some amount of time, which is "infinite" compared to molecular processes.

- So: What gets measured in the lab is the infinite time average $f^*(x_0)$:

$$f^*(x_0) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} f(\phi_t(x_0)) dt$$

- And: For sufficiently chaotic ("ergodic") systems, $\langle f \rangle = f^*(x_0)$.

Def. 6 (Gibbs entropy). The **Gibbs entropy** $S_{\text{Gibbs}}(\rho)$ of an ensemble distribution ρ is the ensemble average of the quantity $-k \ln \rho$:

$$S_{\text{Gibbs}}(\rho) \equiv -k \int_{\Gamma} \rho(x) \ln \rho(x) dx$$

- Compare with "continuous" version of S_{Boltz} :

$$S_{\text{Boltz}}(\Gamma_M) = -Nk \int_{\Gamma_\mu} \rho_\mu(x_\mu) \ln \rho_\mu(x_\mu) dx_\mu$$

- S_{Boltz} is an integral over the *single-particle* phase space Γ_μ of the *constant-energy* subregion Γ_E of Γ .
- S_{Gibbs} is an integral over the full phase space Γ (not even restricted to Γ_E).

However: One can show that S_{Gibbs} reduces to S_{Boltz} for the case of a system of N identical, weakly interacting particles at constant energy...

How S_{Gibbs} relates to S_{Boltz}

- Consider: A system of N identical, weakly interacting particles at constant energy.
- Characterized by distribution given by:

$$\rho(x) = \rho_{\mu}^1(x_{\mu}^1)\rho_{\mu}^2(x_{\mu}^2)\cdots\rho_{\mu}^N(x_{\mu}^N), \quad \text{such that } \rho_{\mu}^i = \rho_{\mu}^j \text{ for all } i, j$$

Weakly interacting particles:
"Total probability" = product
of individual probabilities

Single-particle distribution
for constant-energy
microstates of particle 1

Identical particles: all individual
probabilities are equal

- For this distribution:

$$S_{\text{Gibbs}}(\rho) = -k \int_{\Gamma} \rho_{\mu}^1(x_{\mu}^1)\cdots\rho_{\mu}^N(x_{\mu}^N) \ln[\rho_{\mu}^1(x_{\mu}^1)\cdots\rho_{\mu}^N(x_{\mu}^N)] dx$$

$$= -k \int_{\Gamma_{\mu}^1} \rho_{\mu}^1(x_{\mu}^1) \ln \rho_{\mu}^1(x_{\mu}^1) dx_{\mu}^1 \cdots \int_{\Gamma_{\mu}^N} \rho_{\mu}^N(x_{\mu}^N) dx_{\mu}^N - \cdots$$

$$\Gamma = \Gamma_{\mu}^1 \times \cdots \times \Gamma_{\mu}^N$$

$$dx = dx_{\mu}^1 \cdots dx_{\mu}^N$$

$$- k \int_{\Gamma_{\mu}^1} \rho_{\mu}^1(x_{\mu}^1) dx_{\mu}^1 \cdots \int_{\Gamma_{\mu}^N} \rho_{\mu}^N(x_{\mu}^N) \ln \rho_{\mu}^N(x_{\mu}^N) dx_{\mu}^N$$

$$= -k \int_{\Gamma_{\mu}^1} \rho_{\mu}^1(x_{\mu}^1) dx_{\mu}^1 \ln \rho_{\mu}^1(x_{\mu}^1) - \cdots$$

$$\int_{\Gamma_{\mu}^i} \rho_{\mu}^i(x_{\mu}^i) dx_{\mu}^i = 1$$

$$- k \int_{\Gamma_{\mu}^N} \rho_{\mu}^N(x_{\mu}^N) dx_{\mu}^N \ln \rho_{\mu}^N(x_{\mu}^N)$$

$$= -Nk \int_{\Gamma_{\mu}} \rho_{\mu}(x_{\mu}) \ln \rho_{\mu}(x_{\mu}) dx_{\mu} = S_{\text{Boltz}}(\Gamma_M)$$

Suggests: S_{Boltz} is a
special case of S_{Gibbs}

Two standard Gibbs distributions

- For any given physical system, there can be many different ways to define ρ .
 - Minimally, we want a ρ that is stationary and maximizes S_{Gibbs} .

Def. 7 (Microcanonical distribution). For an isolated system with fixed energy $H(x) = E$, the **microcanonical distribution** ρ_{mc} is given by:

$$\rho_{\text{mc}} = \begin{cases} 1/\Omega(E), & \text{for } H(x) = E \\ 0, & \text{otherwise} \end{cases}$$

Motivation: All microstates with same energy have equal probability

where $\Omega(E) = \int_{\Gamma_E} dx$ is the number of microstates with $H(x) = E$.

Note:

$$\begin{aligned} S_{\text{Gibbs}}(\rho_{\text{mc}}) &= -k \int_{\Gamma} \rho_{\text{mc}}(x) \ln \rho_{\text{mc}}(x) dx \\ &= -k \int_{\Gamma_E} (1/\Omega(E)) \ln [1/\Omega(E)] dx \\ &= -k(1/\Omega(E)) \ln [1/\Omega(E)] \int_{\Gamma_E} dx \\ &= k \ln \Omega(E) \end{aligned}$$

A measure of the number of microstates of the system

S_{Boltz} as a special case of S_{Gibbs} . Part II:
The Boltzmann entropy $S_{\text{Boltz}}(\Gamma_M)$ of a macrostate of an isolated N -particle system at constant energy can be thought of as the Gibbs entropy $S_{\text{Gibbs}}(\rho_{\text{mc}})$ of the microcanonical distribution for an ensemble of N weakly interacting systems.

Def. 8 (*Canonical distribution*). For a non-isolated system S in equilibrium with a heat bath R at fixed temperature T and fixed *total* energy $H(x) = E = E_R + E_S$, $E_S \ll E$, the **canonical distribution** ρ_c is given by:

$$\rho_c(x) = Z^{-1} e^{-\beta H(x)}$$

where $Z = \int e^{-\beta H(x)} dx$, and $\beta = 1/T$.

- Note:

$$\begin{aligned} S_{\text{Gibbs}}(\rho_c) &= -k \int_{\Gamma} \rho_c(x) \ln \rho_c(x) dx \\ &= \int_{\Gamma} \rho_c [-k \ln (e^{-\beta H(x)} / Z)] dx \\ &= \int_{\Gamma} \rho_c [-k (\ln e^{-\beta H(x)} - \ln Z)] dx \\ &= \int_{\Gamma} \rho_c [k\beta H(x) + k \ln Z] dx \\ &= k\beta \langle H \rangle + k \ln Z \int_{\Gamma} \rho_c dx \\ &= k\beta \langle H \rangle + k \ln Z \quad \leftarrow \int_{\Gamma} \rho_c dx = 1 \end{aligned}$$

S_{Boltz} as a special case of S_{Gibbs} . Part III:
The Gibbs canonical distribution ρ_c is the generalization of the Maxwell-Boltzmann distribution for a single system to an ensemble of systems consisting of one in equilibrium with the rest.

Interpretive Issues:

- (1) *Why* do low-probability states evolve into high-probability states? What justifies a given stationary, S_{Gibbs} -maximizing distribution $\rho(x, t)$?
 - *Characterizations of the dynamics are, again, required to justify this.*

- (2) *How* are the probabilities to be interpreted?
 - (a) *Ontic probabilities* = properties of physical systems
 - *Long run frequencies?*
 - *Single-case propensities?*

 - (b) *Epistemic probabilities* = measures of degrees of belief
 - *Objective (rational) degrees of belief?*
 - *Subjective degrees of belief?*

(3) How should the approach to equilibrium be understood?

- A Gibbs distribution $\rho(x)$ is required to be stationary. *constant in time!*

So how can the Gibbs entropy $S_{\text{Gibbs}}(\rho)$ increase?

Standard response: Coarse-grain it!

- Partition phase space Γ into cells ω each of size $\delta\omega$.
- For any ρ , define a coarse-grained version ρ_{coarse} by:

$$\rho_{\text{coarse}}(x) \equiv \frac{1}{\delta\omega} \int_{\omega(x)} \rho(x') dx'$$

Just like Boltzmann coarse-graining, except on Γ and not Γ_μ

ρ_{coarse} assigns to every state x in cell ω the average of the values that ρ assigns to all states in ω .

Claim 1. $S_{\text{Gibbs}}(\rho_{\text{coarse}}) \geq S_{\text{Gibbs}}(\rho)$

Claim 2. Under various assumptions (ergodicity, "molecular randomness", etc.), for $t_1 > t_0$,

$$S_{\text{Gibbs}}(\rho_{\text{coarse}})|_{t=t_1} \geq S_{\text{Gibbs}}(\rho_{\text{coarse}})|_{t=t_0}$$

Task: Justify these assumptions!