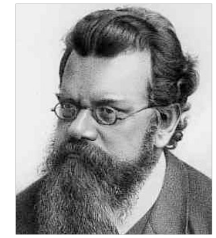
04a. Entropy in Statistical Mechanics: Boltzmann

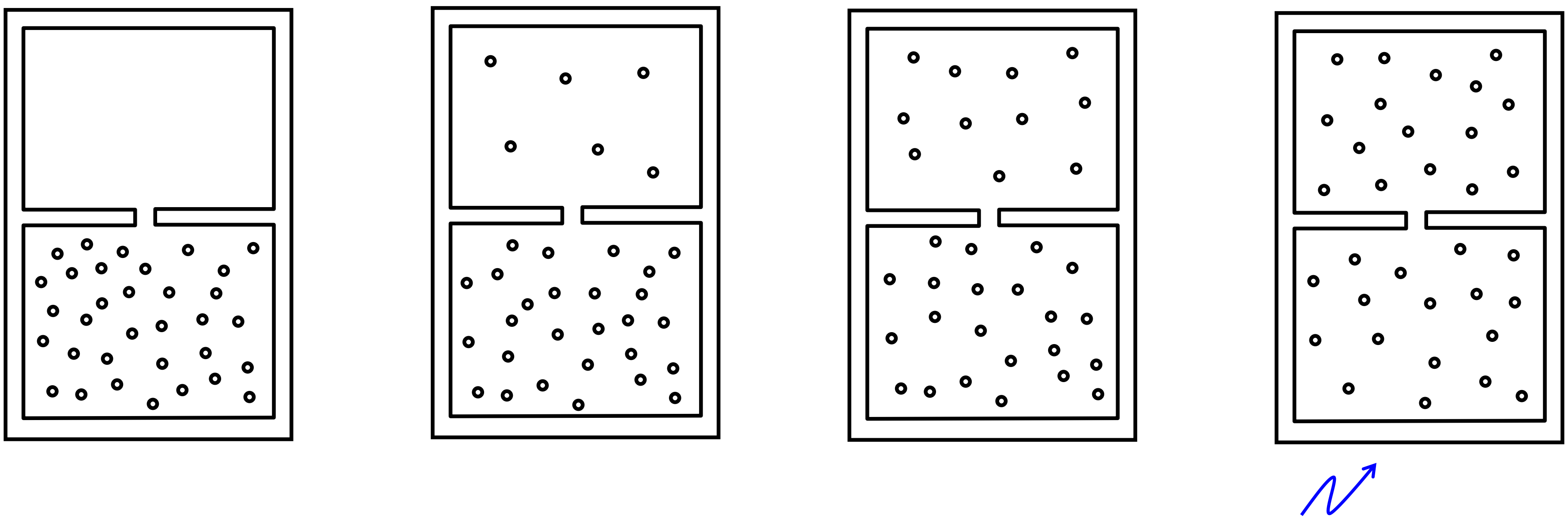


Ludwig Boltzmann
(1844-1906)

- *<u>Goal</u>*: To explain the behavior of *macroscopic* systems in terms of the dynamical laws governing their *microscopic* consituents.
  - *To provide a micro-dynamical explanation of the Minus 1st and 2nd Laws.*

1. Boltzmann Entropy S_{Boltz}

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



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

- *Equilibrium macrostate = state characterized by thermodynamic properties (temp, volume, pressure, etc.) that do not change with time.*
- *Maximizes S_{TD}!*

- 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.

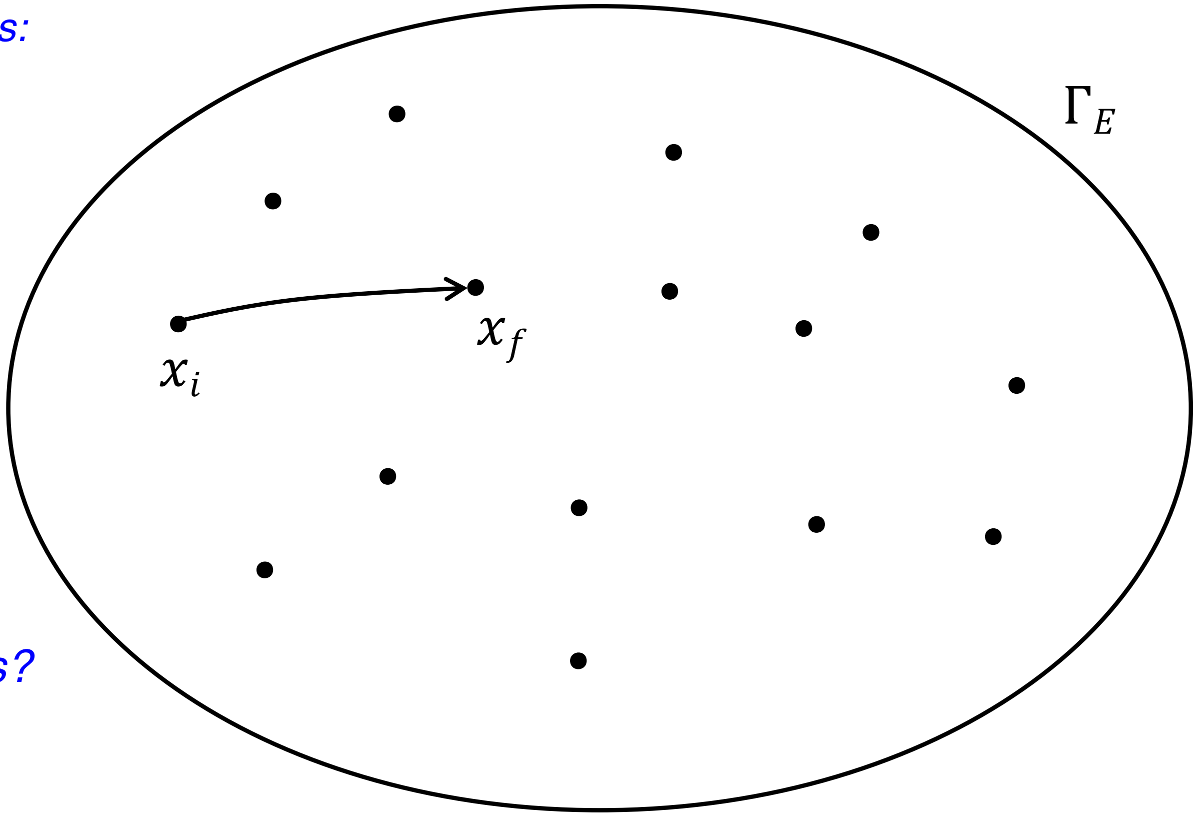
Let Γ = *phase space* = $6N$-dim space of all possible microstates.

Let Γ_E = region of Γ that consists of all microstates with constant energy E.

A point x in Γ_E is labeled by $6N$ numbers:

$$x = (x^{(1)}, y^{(1)}, z^{(1)}, p_x^{(1)}, p_y^{(1)}, p_z^{(1)}, \dots ,$$
$$x^{(N)}, y^{(N)}, z^{(N)}, p_x^{(N)}, p_y^{(N)}, p_z^{(N)})$$

Hamiltonian dynamics maps initial microstate x_i to final microstate x_f.



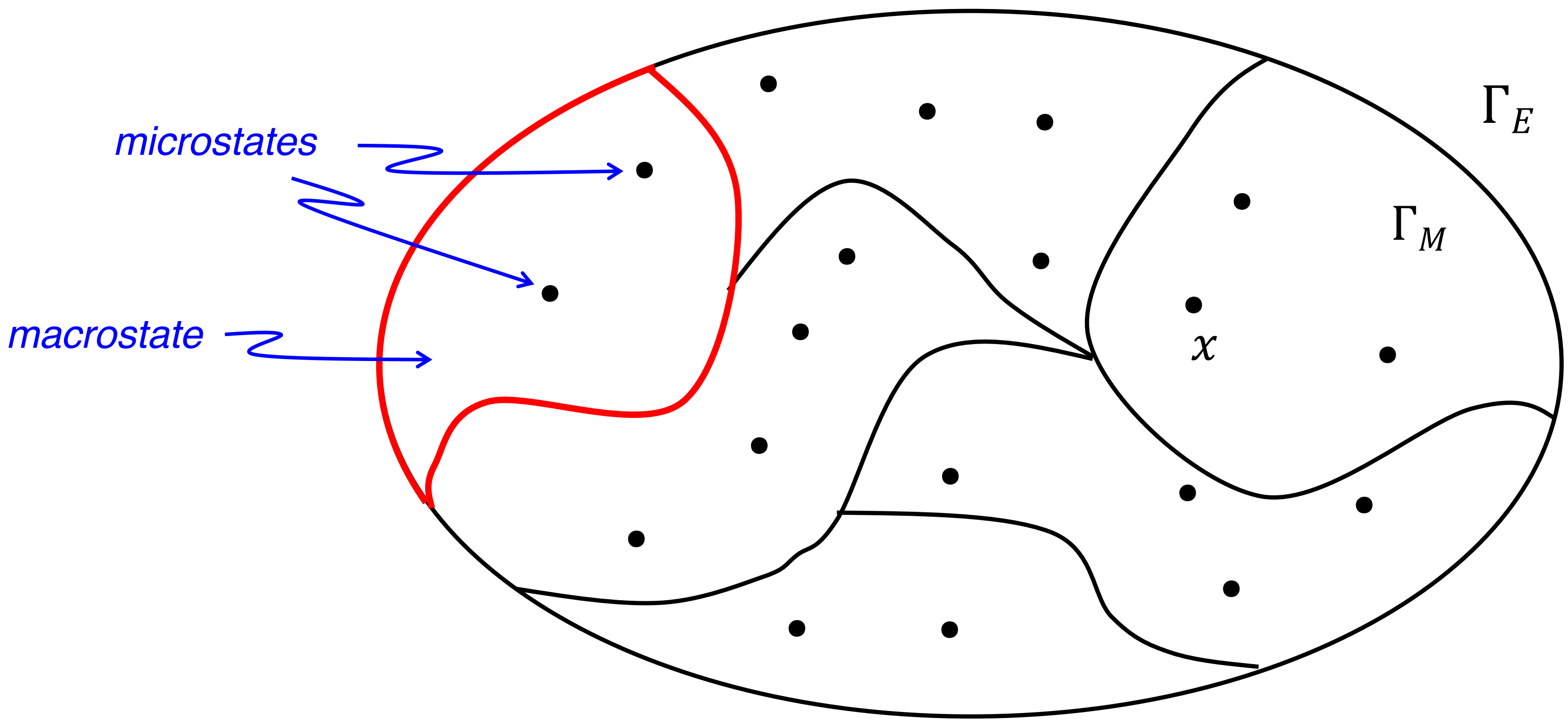
Can Minus 1st and 2nd Laws be explained in terms of this dynamics?

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*:

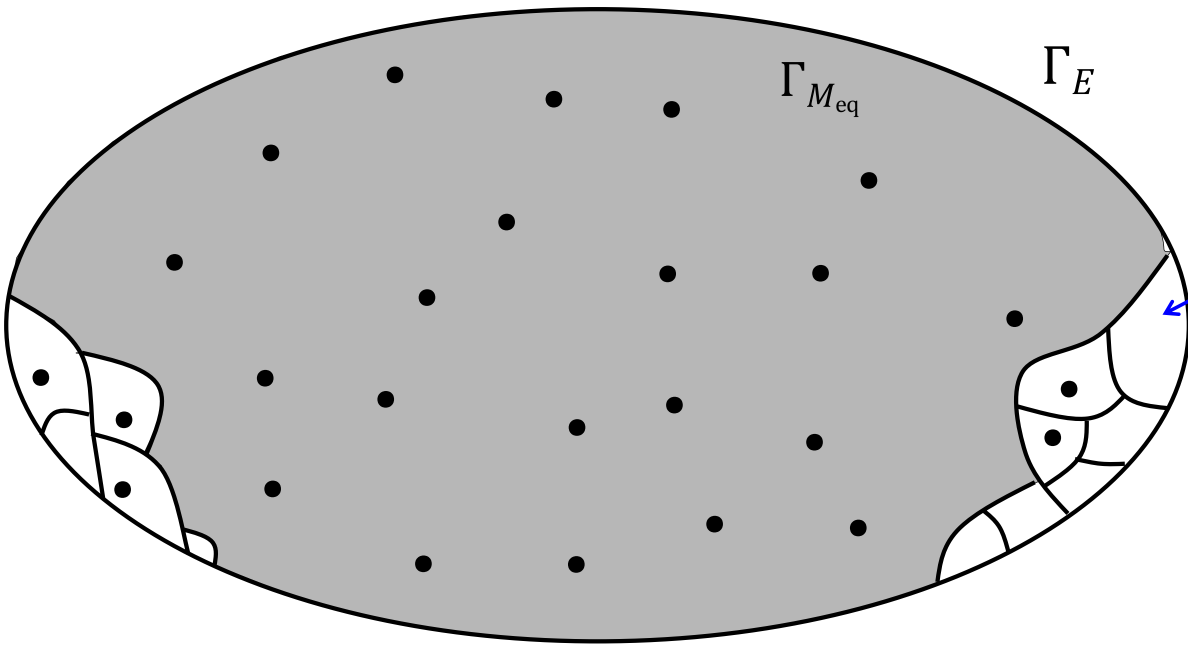
- To each microstate there corresponds exactly one macrostate.
- Many distinct microstates can correspond to the same macrostate.

- *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 $\Gamma_{M_{\text{eq}}}$ is *much larger* than any other macrostate.

But why?



very small non-equilibrium macrostates

$S_{\text{Boltz}}(\Gamma_M)$ *obtains its maximum value for* $\Gamma_{M_{\text{eq}}}$

Def. 3 (*Boltzmann entropy*). The **Boltzmann entropy** $S_{\text{Boltz}}(\Gamma_M)$ of a macrostate Γ_M of a thermally isolated physical system at constant energy is given by $S_{\text{Boltz}}(\Gamma_M) \equiv k \ln|\Gamma_M|$, 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 $\Gamma_{M_{\text{eq}}}$ 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 of microstates* Goldstein (2001)

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

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

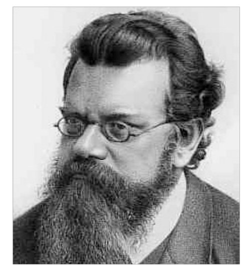
- *But*: What is it about the *dynamics* that evolves atypical states to typical states?
  - "If a system is in an atypical microstate, it does not evolve into an equilibrium microstate *just because* the latter is typical." (Frigg 2009)
- Need to identify properties of the dynamics that guarantee atypical 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)

Frigg, R. (2009) 'Typicality and the Approach to Equilibrium in Boltzmannian Statistical Mechanics', *Philosophy of Science 76*, 997-1008.

(b) *Appeal to probability of macrostates*

Claim. A system approaches equilibrium because it evolves from low probability macrostates to high probability macrostates, and the equilibrium macrostate has the highest probabililty.

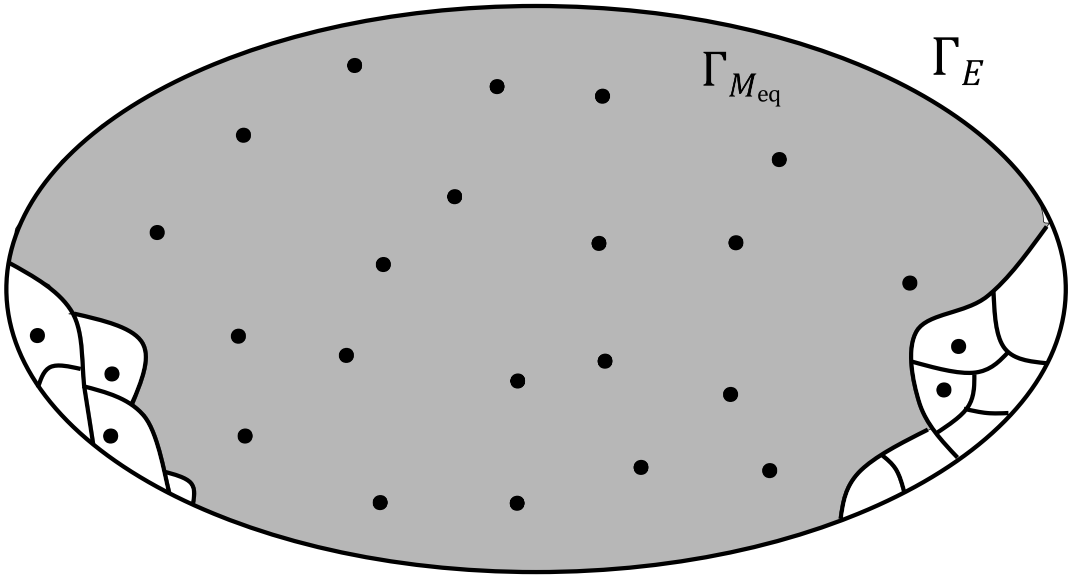
"In most cases, the initial state will be a very unlikely state. From this state the system will steadily evolve towards more likely states until it has finally reached the most likely state, i.e., the state of thermal equilibrium."



- *Task*: Come up with a way to assign probabilites to macrostates such that the larger the macrostate, the greater the probability of finding a microstate in it.

Story to come: Associate the probability of a macrostate with the number of microstates it contains!

<u>But</u>: What determines the number of microstates in a macrostate?



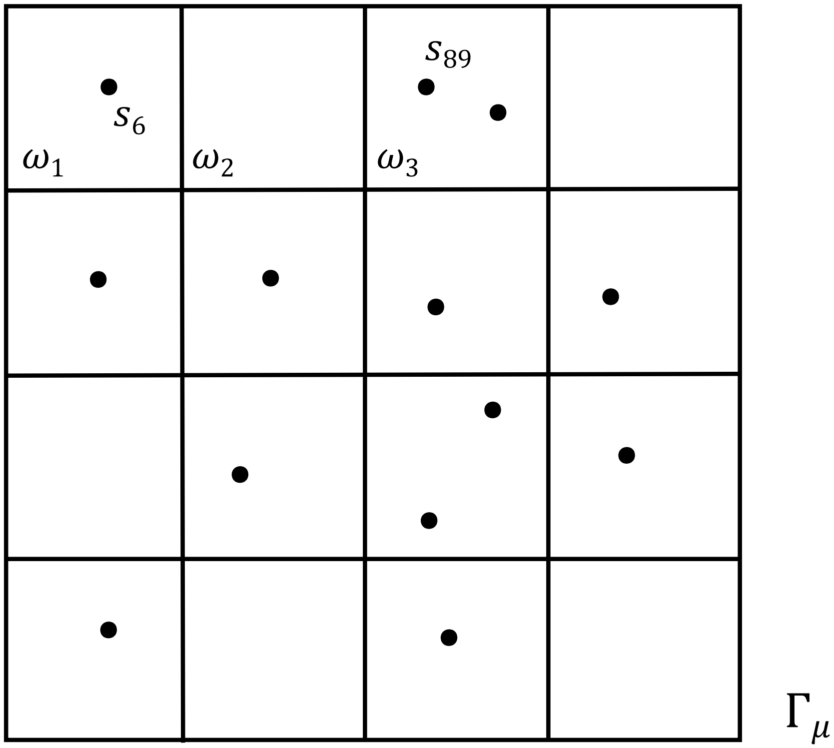
- *If we had a measure function defined on Γ (i.e., a "density" function), then we could use it to calculate the number of points in a given macrostate region.*

Gibbs' approach!

- *<u>Boltzmann's approach</u>*:
  - A point in a macrostate region of Γ_E is an N-particle microstate, and it corresponds to N points in a *single-particle phase space*, call it Γ_μ.
  - A macrostate region of Γ_E corresponds to a *distribution* of N single-particle microstates.
  - The number of points in a macrostate region then is the number of possible ways to arrange N single-particle microstates with respect to the corresponding *single-particle distribution!*

To define this thing, Boltzmann coarse-grains the single-particle phase space...

Coarse-graining the single-particle phase space



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

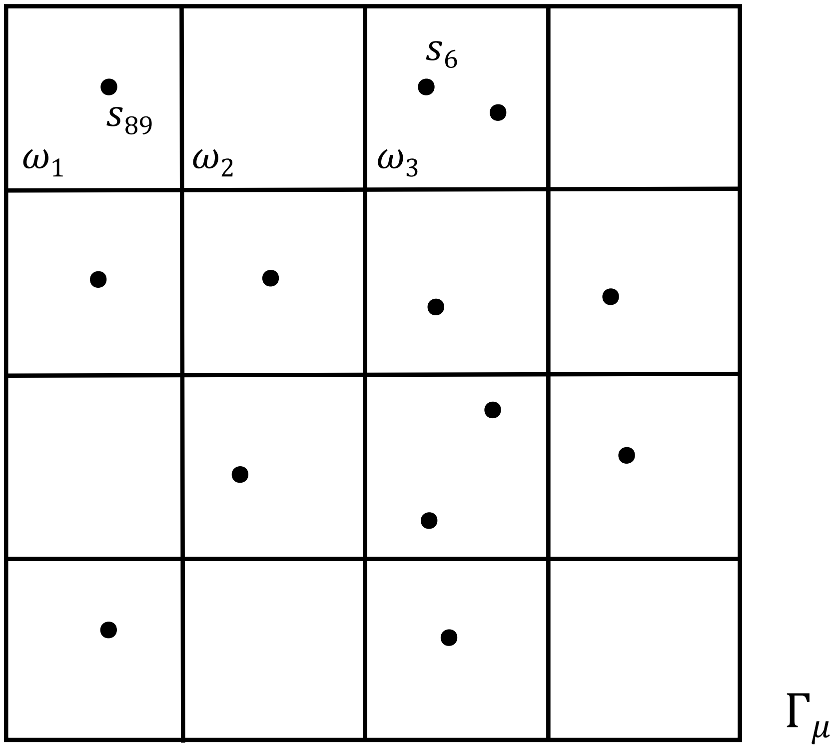
- Start with the *6-dim* phase space Γ_μ of a single particle.
- Partition Γ_μ into ℓ cells $\omega_1, \ldots, \omega_\ell$ of volume $\Delta\omega = \Delta x^3 \Delta p^3$.
- A microstate of an N-particle system is given by N points in Γ_μ.

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

N points in Γ_μ correspond to one point in Γ_E

Def. 4. An **arrangement** is a specification of *which* single-particle microstates lie in which cells.

Coarse-graining the single-particle phase space



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

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

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

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 $\omega_1, \ldots, \omega_\ell$ of volume $\Delta\omega = \Delta x^3 \Delta p^3$.
- A microstate 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

N points in Γ_μ correspond to one point in Γ_E

Def. 4. An **arrangement** is a specification of *which* single-particle microstates lie in which cells.

Def. 5. A **single-particle distribution** $D = (n_1, n_2, \ldots, n_\ell)$ is a specification of *how many* single-particle microstates (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 $D = (n_1, n_2, ..., n_\ell)$?

- *Answer*:

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

$n! = n(n-1)(n-2)\cdots 1$
$= \#$ *of ways to arrange n distinguishable objects*
$0! = 1$

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

$$G(D_1) = \frac{N!}{N!} = 1$$

← *Only one way for all N particle states to be in ω_1.*

$$G(D_2) = \frac{N!}{(N-1)!} = \frac{N(N-1)(N-2)\cdots 1}{(N-1)(N-2)\cdots 1} = N$$

← *There are N different ways ω_2 could have one state in it; namely, if s_1 was in it, or if s_2 was in it, or if s_3 was in it, etc..*

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

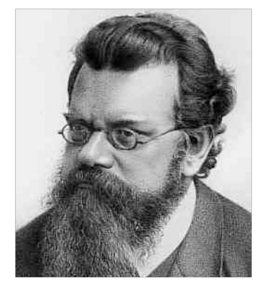
- *Answer*:

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

$n! = n(n-1)(n-2)\cdots 1$
$= \#$ *of ways to arrange n distinguishable objects*
$0! = 1$

Assumption 1. The *probability* of a single-particle 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 $G(D)$.

Assumption 2. Each single-particle 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 (multi-particle microstate) in Γ_E corresponds to an arrangement of single-particle microstates in 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 $|\Gamma_{M_D}| = \left[\begin{array}{l}\textit{\# arrangements} \\ \textit{compatible with } D\end{array}\right] \times \left[\begin{array}{l}\textit{volume} \\ \textit{element of } \Gamma_E\end{array}\right]$

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

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

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

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

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

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

Other formulations of S_{Boltz}:

$$\begin{aligned} S_{\text{Boltz}}(\Gamma_{M_D}) &= k\ln(G(D)) + \text{const.} \\ &= k\ln\left(\frac{N!}{n_1!\cdots n_\ell!}\right) + \text{const.} \\ &= k\ln(N!) - k\ln(n_1!) - \cdots - k\ln(n_\ell!) + \text{const.} \\ &\approx (Nk\ln N - N) - (n_1 k\ln n_1 - n_1) - \cdots - (n_\ell k\ln n_\ell - n_\ell) + \text{const.} \\ &= \boxed{-k\sum_{i=1}^{\ell} n_i \ln n_i + \text{const.}} \end{aligned}$$

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

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

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

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

  Probabilities for single-particle microstates (not macrostates)!

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

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

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

  single-particle probability distribution over Γ_μ

2. The Maxwell-Boltzmann Equilibrium Distribution

- What distribution $D^* = (n_1^*, ..., n_\ell^*)$ 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 single-particle microstates

- 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 to n_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...

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

$$\text{(a)}\ \sum_{i=1}^{\ell} n_i = N \qquad \text{(b)}\ \sum_{i=1}^{\ell} \varepsilon_i n_i = U$$

- Enforce (a) on n_i^*

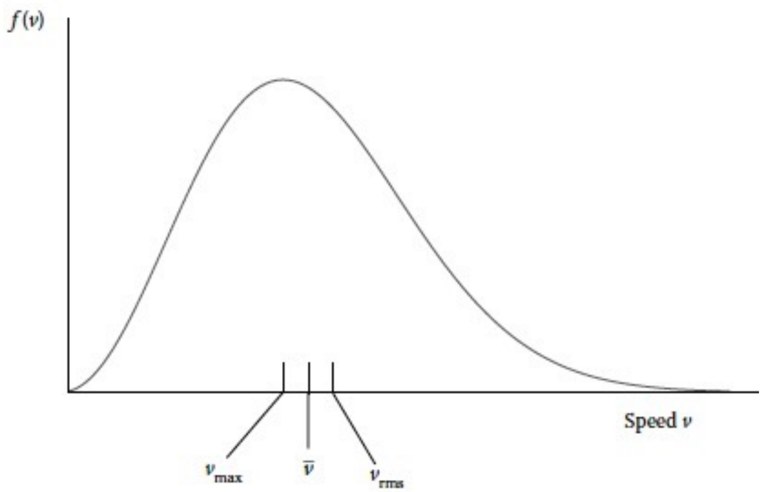
$$\sum_i n_i^* = N = e^{-\alpha/k}\sum_i e^{-\beta\varepsilon_i/k} \quad \text{or} \quad e^{-\alpha/k} = N/Z, \quad Z \equiv \sum_i e^{-\beta\varepsilon_i/k}$$

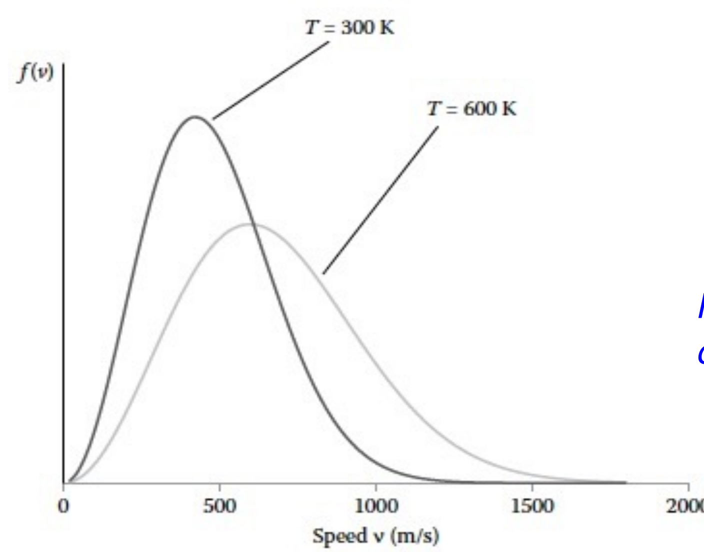
- So: $n_i^* = (N/Z)e^{-\beta\varepsilon_i/k}$

The "Maxwell-Boltzmann distribution"

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

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





M-B distribution in terms of velocity (with $\beta = 1/T$)

3. Boltzmann Entropy S_{Boltz} vs. Thermodynamic Entropy S_{TD}

Attempt #1

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

Macroscopic point of view	*Microscopic point of view*
$dU = \delta Q + \delta W$	$dU = d(\sum_i \varepsilon_i n_i)$
$= TdS_{\text{TD}} - PdV$	$= \sum_i \varepsilon_i dn_i + \sum_i n_i d\varepsilon_i$

Assume:
- A change in V is related to a change in single-particle energies ε_i.
- A change in S_{TD} is related to a change in microstate number n_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 $n_i^* = \frac{N}{Z} e^{-\beta\varepsilon_i/k}$:

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

$$= \beta\sum_i \varepsilon_i dn_i$$

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

- *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.

    Just another way of assuming that the largest macrostate is the equilibrium macrostate.

  - Assumes a change in S_{TD} is related to a change in microstate number n_i.

    Isn't this what we're trying to show (i.e., $S_{\text{TD}} = S_{\text{Boltz}}$)?

  - 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?*

Attempt #2

Claim. $\Delta S_{\text{Boltz}} = \Delta S_{\text{TD}}$ for free expansion of an ideal gas.

- *Macroscopic point of view*
  - Irreversible: $W = 0, T = \text{const.}, \ \Delta U = 0.$
  - Reversible: $\delta W = -PdV, T = \text{const.}, \ \Delta U = 0.$

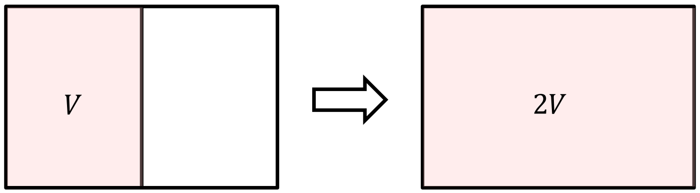
$$dS_{\text{TD}} = \delta Q/T$$
$$= (P/T)dV$$
$$= (nR/V)dV$$

$\delta Q = dU - \delta W$
$= 0 + PdV$

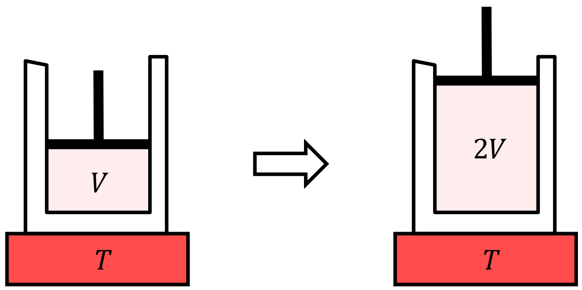
$PV = nRT$

$n = \#\text{moles}$
$R = \text{const.}$

$$\Delta S_{\text{TD}} = nR\int_V^{2V} \frac{dV}{V} = nR\ln 2$$



irreversible free expansion



reversible free expansion

- *Microscopic point of view*
  - N = number of gas particles.
  - Ω = # arrangements of single-particle microstates before expansion.

Claim. $2^N\Omega$ = # arrangements of single-particle microstates after expansion.

Why?
- Each cell in coarse-grained Γ_μ has volume $\Delta p^3 \Delta x^3$.
- *During expansion*:
  - Momentum part doesn't change. ← *T = const. = ave. kinetic energy $= \frac{1}{2m}\overline{p^2}$*
  - Position part changes, since volume doubles.
- *After expansion*:
  - Each particle has twice as many possible single-particle position microstates it can be in; so for N particles, there are 2^N as many possible single-particle position microstates.

- *So*:

$$\Delta S_{\text{Boltz}} = k\ln(2^N\Omega) - k\ln\Omega = k\ln 2^N = Nk\ln 2 = nR\ln 2$$

Same expression as ΔS_{TD}!

What this shows:

- For the free expansion of an ideal gas, it is consistent to identify ΔS_{TD} with $\Delta S_{\mathrm{Boltz}}$.

- *But*:
  - For this particular physical system, ΔS_{TD} and $\Delta S_{\mathrm{Boltz}}$ take the same value.

    Does this necessarily entail they measure the same quantity?

  - 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?*

Attempt #3

Claim. $S_{\text{Boltz}} = S_{\text{TD}}$ for an ideal gas.

- *Macroscopic point of view*

$$dU = \delta Q + \delta W = T dS_{\text{TD}} - P dV$$

1st Law for reversible process

$$dS_{\text{TD}} = dU/T + (P/T)dV$$
$$= (C_V/T)dT + (nR/V)dV$$

Constant volume heat capacity

$C_V \equiv (\partial U/\partial T)_V$

$= dU/dT$, for $U = U(T)$

- *Or*:

$$ds_{\text{TD}} = (c_v/T)dT + (R/v)dv$$

Molar quantities

$s_{\text{TD}} = S_{\text{TD}}/n$

$c_v = C_V/n$

$v = V/n$

Def. The **heat capacity** C of a physical system is the amount of absorbed heat δQ needed to change the temperature of the system by dT: $C \equiv \delta Q/dT$.

- *So*:

$$s_{\text{TD}} = c_v \ln T + R \ln v + \text{const.}$$

- *Microscopic point of view*
  - What is S_{Boltz} of a macrostate of an ideal gas with N particles at temp T, heat capacity C_V, volume V?
  - Need to first determine number of possible microstates Ω it can be in.

Claim. $\Omega = \Omega_{\text{position}}\Omega_{\text{momentum}} = [V/\Delta x^3]^N [p^3_{\text{rms}}/\Delta p^3]^N$

Position multi-particle microstates Ω_{position}

- V = region in Γ_μ.
- $V/\Delta x^3$ = # occupied cells in V.
  = coarse-grained # position single-particle microstates in V.
- $[V/\Delta x^3]^N$ = coarse-grained # position multi-particle microstates.

Momentum multi-particle microstates Ω_{momentum}

- $p_{\text{rms}} \equiv (\overline{p^2})^{1/2}$ = root mean square momentum. ← *What gets measured:* Ave. kinetic energy $= \frac{1}{2m}\overline{p^2} = \frac{1}{2m}p^2_{\text{rms}}$
- $p^3_{\text{rms}}/\Delta p^3$ = # occupied cells in region of single-particle momentum phase space.
  = coarse-grained # momentum single-particle microstates.
- $[p^3_{\text{rms}}/\Delta p^3]^N$ = coarse-grained # momentum multi-particle microstates.

- *Now simplify Ω*

$$\Omega_{\rm pos}\Omega_{\rm mo} = [V/\Delta x^3]^N [p_{\rm rms}^3/\Delta p^3]^N = [p_{\rm rms}^3 V/\Delta x^3 \Delta p^3]^N$$

$$= \frac{1}{N!}\left[\frac{p_{\rm rms}^3 V}{(\Delta x \Delta p)^3}\right]^N$$

← *Assume indistinguishable particles, so need "overcount" correction factor* $1/N!$

$$\approx \left[\frac{eVp_{\rm rms}^3}{N(\Delta x \Delta p)^3}\right]^N$$

← *Stirling's approx:* $N! \approx (N/e)^N$*, for large* N

$$= \left[\frac{eV(2mU)^{3/2}}{N^{5/2}(\Delta x \Delta p)^3}\right]^N$$

← $p_{\rm rms} = (\overline{p^2})^{1/2}$

$= \left(\sum_i p_i^2/N\right)^{1/2}$

$= (2mU/N)^{1/2}$ ← *Assume weakly interacting: Total* U *= sum of single-particle* U*'s.*

$$= \left[\frac{eV(2mU)^{3/2}}{N^{5/2}h^3}\right]^N$$

← *quantum hypothesis:* $\Delta x \Delta p = h$

$$= \left[\frac{eV(2mU)^{3/2}}{(nN_A)^{5/2}h^3}\right]^{nN_A}$$

← $N = nN_A$, n *= #moles,* N_A *= Avogadro's number*

$$= \left\{\left(\frac{V}{n}\right)\left(\frac{U}{n}\right)^{3/2}\left[\frac{e(2m)^{3/2}}{N_A^{5/2}h^3}\right]\right\}^{nN_A}$$

- Can now calculate S_{Boltz}!

$$S_{\text{Boltz}} = k\ln\Omega \;=k\ln\left\{\left(\frac{V}{n}\right)\left(\frac{U}{n}\right)^{3/2}\left[\frac{e(2m)^{3/2}}{N_A^{5/2}h^3}\right]\right\}^{nN_A}$$

$$= nkN_A\left[\ln\left(\frac{V}{n}\right)+\tfrac{3}{2}\ln\left(\frac{U}{n}\right)+\text{const.}\right]$$

- *Or*:

$$s_{\text{Boltz}} = R\,[\ln v + \tfrac{3}{2}\ln u + \text{const.}]$$

$$= R\ln v + \tfrac{3}{2}R\ln T + \text{const.}$$

$$= R\ln v + c_v \ln T + \text{const.}$$

Molar quantities
$s_{\text{Boltz}} = S_{\text{Boltz}}/n,\ v = V/n,\ u = U/n$

Ideal monotomic gas
$u = \tfrac{3}{2}RT$
$c_v = \tfrac{3}{2}R$

- *So*:

$$s_{\text{Boltz}} = R\ln v + c_v\ln T + \text{const.}$$

Same expression as s_{TD}!

What this shows:

- S_{TD} and S_{Boltz}. take the same value for an N particle gas under the following assumptions:
  (i) The gas particles are indistinguishable.
  (ii) N is very large (Stirling's approx.).
  (iii) The gas particles are weakly interacting.
  (iv) The gas particles obey the (quantum) uncertainty relation $\Delta x \Delta p = h$.
  (v) The gas is monatomic.
  (vi) The gas obeys the ideal gas law.

- *But (again)*:
  - Does this mean S_{TD} and S_{Boltz} measure the same quantity?
  - S_{TD} absolutely obeys 2nd Law, while S_{Boltz} does not.