

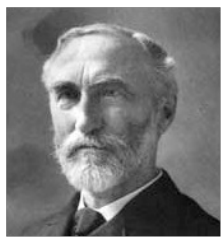
04b. Entropy in Statistical Mechanics: Gibbs

1. Gibbs' Approach

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- 2. Gibbs Entropy S_{Gibbs}
- 3. S_{Gibbs} vs. S_{Boltz}
- 4. Interpretive Issues

Boltzmann: Analysis of a *single* multiparticle system.

- Point x in Γ_E : microstate of system.
- Function f on Γ_E : a property of the system in terms of its micro-properties (positions/momenta of its particles).



Willard Gibbs
(1839-1903)

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 !

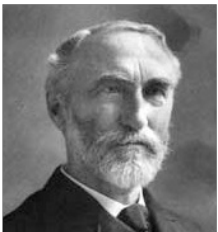
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Gibbs: Analysis of an *ensemble* of infinitely many copies of same system.

- 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.

- A "density" function: tells you how the points in Γ are spread out.
- 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."*

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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?

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Roles for $\rho(x)$:

- Assigns probabilities to microstates: $\int_S \rho(x) dx$  Probability of finding microstate x in region S
- Determines ensemble averages: $\langle f \rangle \equiv \int_\Gamma f(x) \rho(x) dx$  Represents a measurable property.
- Defines notion of equilibrium.

ρ is an *equilibrium state* just when it is stationary (i.e., constant in time).

 $\langle f \rangle$ is constant just when ρ is stationary.

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Key differences

- *Boltzmann*: No distribution defined on Γ_E ; Γ_E divided into macrostate regions; equilibrium state defined as largest macrostate region.
- *Gibbs*: Distribution defined on Γ ; no reference to macrostates; equilibrium state defined in terms of a property (stationarity) of a distribution.

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, $\langle f \rangle = f^*(x_0)$.

2. Gibbs Entropy S_{Gibbs}

Def. 1 (*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...

3. Gibbs Entropy S_{Gibbs} vs. Boltzmann Entropy 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. 2 (*Microcanonical distribution*). For an isolated system with fixed energy $H(x) = E$, the **microcanonical distribution** ρ_{mc} is given by:

$$\rho_{\text{mc}} = \begin{cases} 1/\Omega(E), & \text{for } H(x) = E \\ 0, & \text{otherwise} \end{cases} \quad \leftarrow \text{Motivation: All microstates with same energy have equal probability}$$

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

- Note:

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

$\leftarrow$ 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. 3 (*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.

4. Interpretive Issues

- (1) *Why* do low-probability states evolve into high-probability states? What justifies a given stationary, S_{Gibbs} -maximizing distribution $\rho(x)$?
 - *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 constant in time.  entailed by Liouville's Theorem

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

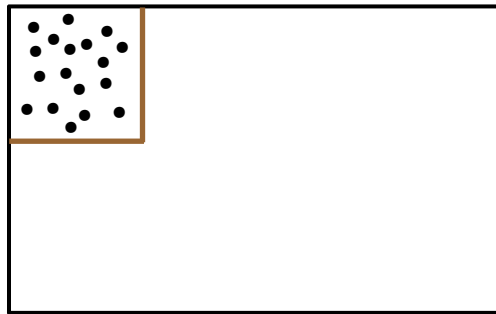
Claim 2. Under various assumptions (ergodicity, "molecular randomness", etc.), for $t_1 > t_0$,

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

 Task: Justify these assumptions!

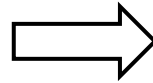
(4) Can S_{Gibbs} and/or S_{Boltz} be interpreted as a measure of "disorder"?

- Idea: $S_{\text{Boltz}}(\Gamma_M) = S_{\text{Gibbs}}(\rho_{\text{mc}}) = k \ln \Omega$ is a measure of the number Ω of possible microstates of a system in a macrostate Γ_M (Boltzmann), or characterized by a microcanonical Gibbs distribution (Gibbs).
- And: Ω reflects the system's "order": The greater Ω is, the less-ordered the system is.

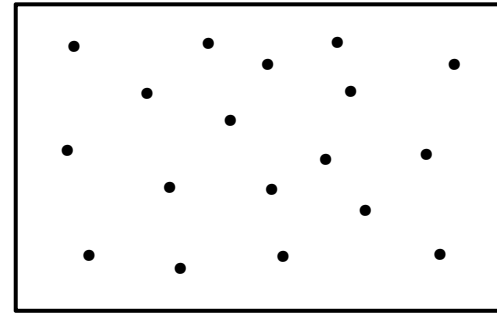


- Initial equilibrium state: particles located behind partition in small region of chamber.
- Ω_i given by small range of position values and some given range of momentum values.

More ordered?



initial constraints removed



- Final equilibrium state: particles evenly distributed throughout chamber.
- Ω_f given by larger range of position values and same range of momentum values.

Less ordered?

- But: Why should initial state be thought of as more ordered?

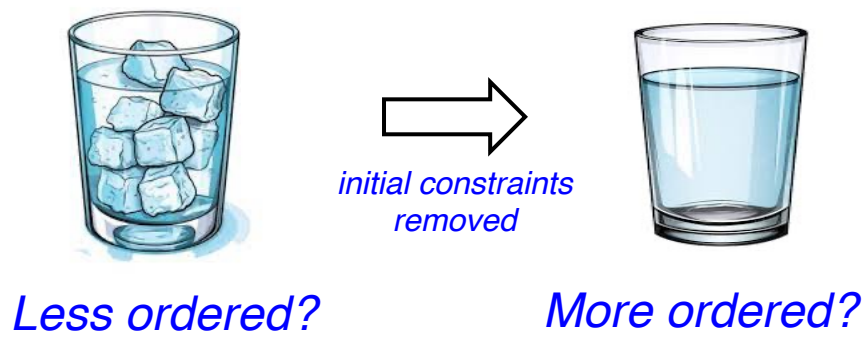
- Counter-example #1:

- Initial state: *Disorderly* protesters behind police barricades.
- Final state: *More orderly* protesters allowed to march down street.

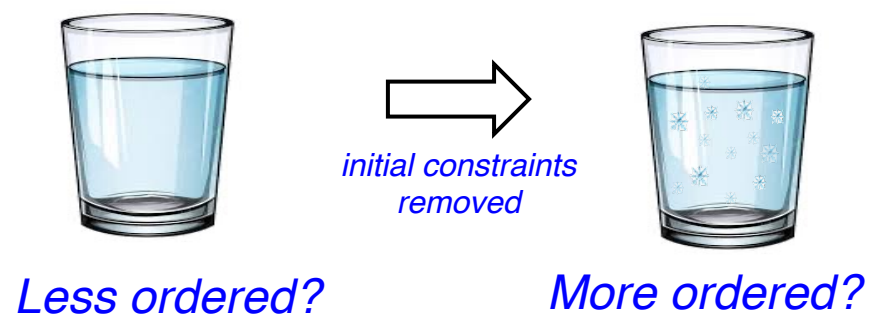


More constrained? But final state is constrained equilibrium state, too (just different constraints).

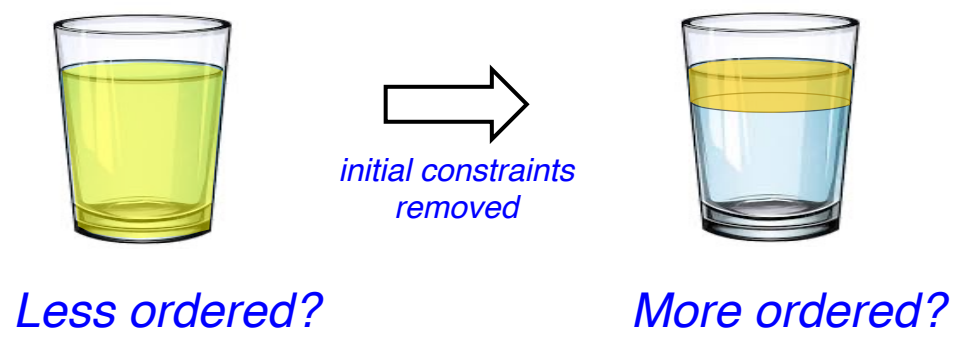
- Counter-example #2: Ice cubes melting in water.
- Initial state: *Disorderly* mixture of irregular-shaped ice cubes floating in liquid water.
- Final state: *More orderly* homogeneous transparent liquid.
- $\Omega_i < \Omega_f$



- Counter-example #3: Crystalization of supercooled water.
- Initial state: *Disorderly* supercooled water at temp $\ll 0^\circ\text{C}$.
- Final state: *More orderly* ice
- $\Omega_i < \Omega_f$



- Counter-example #4: Separation of oil and water.
- Initial state: *Disorderly* emulsion of water/oil.
- Final state: *More orderly* separation of water and oil into distinct layers.
- $\Omega_i < \Omega_f$



Moral: "Order" isn't necessarily a reflection of a system's possible microstates.