13. The Kinetic Theory, Part 2: Objections.

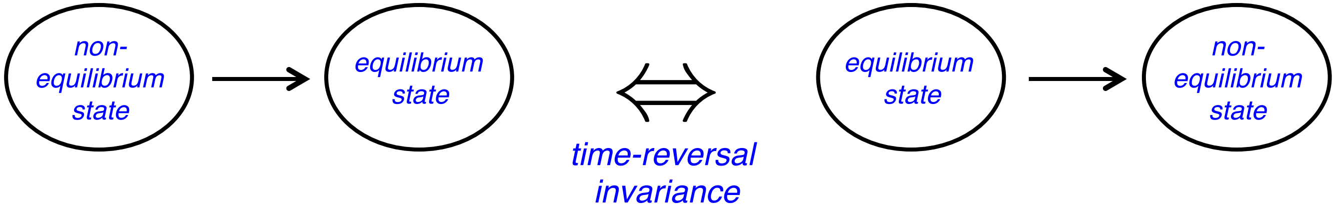
1. Loschmidt's *Umkehreinwand* (Reversibility Objection) (1876).

"Über die Zustand des Wärmegleichgewichtes eines Systems von Körpern mit Rucksicht auf die Schwerkraft."

Josef Loschmidt
(1821-1895)

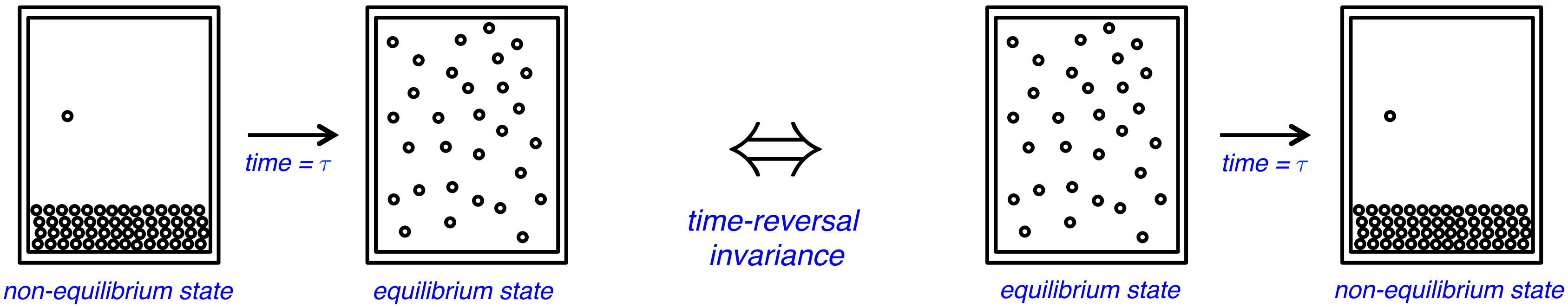
- *H*-Theorem implies that a gas in any non-equilibrium velocity distribution will move towards the equilibrium distribution and then stay there.
  - <u>*But*</u>: *The underlying laws of mechanics for the particles are time-reversal invariant.*

- <u>*Time-reversal invariance implies*</u>: For any equilibrium state of a gas that has evolved from a non-equilibrium state, there corresponds an equilibrium state that will evolve to a non-equilibrium state.



- <u>*Thus*</u>: The *H*-Theorem is incompatible with the underlying laws of mechanics.

- *Ex*: Gas in container in initial state in which all atoms but one lie at rest on bottom.
  - *Single moving atom collides with atoms at rest, eventually resulting in a stationary (equilibrium) state characterized by the Maxwell-Boltzmann distribution.*
  - *Time-reversed system should also be possible: initial equilibrium state eventually evolving into a state in which all atoms but one lie at rest on bottom.*



"Indeed, if in the above case, after a time τ which is long enough to obtain the stationary state, one suddenly assumes that the velocities of all atoms are reversed, we would obtain an initial state that would appear to have the same character as the stationary state. For a fairly long time this would be appropriate, but gradually the stationary state would deteriorate, and after passage of the time τ we would inevitably return to our initial state: only one atom has absorbed all kinetic energy of the system..., while all other molecules lie still on the bottom of the container... Obviously in every arbitrary system the course of events must be become retrograde when the velocities of all its elements are reversed."

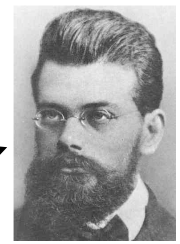
Boltzmann's Response, Part 1 (1877a)

"On the Relation of a General Mechanical Theorem to the 2nd Law of Thermodynamics"

- How can the *H*-Theorem be understood in light of the clear truth of the time reversibility of the underlying micro-mechanics?

"Indeed it is clear that any individual uniform distribution, which might arise after a certain time from some particular initial state, is just as improbable as an individual non-uniform distribution; just as in the game of Lotto, any individual set of five numbers is an improbable as the set 1, 2, 3, 4, 5. It is only because there are many more uniform distributions than non-uniform ones that the distribution of states will become uniform in the course of time."

"One therefore cannot prove that, whatever may be the positions and velocities of the spheres at the beginning, the distribution must become uniform after a long time; rather one can only prove that infinitely many more initial states will lead to a uniform one after a definite length of time than to a non-uniform one."

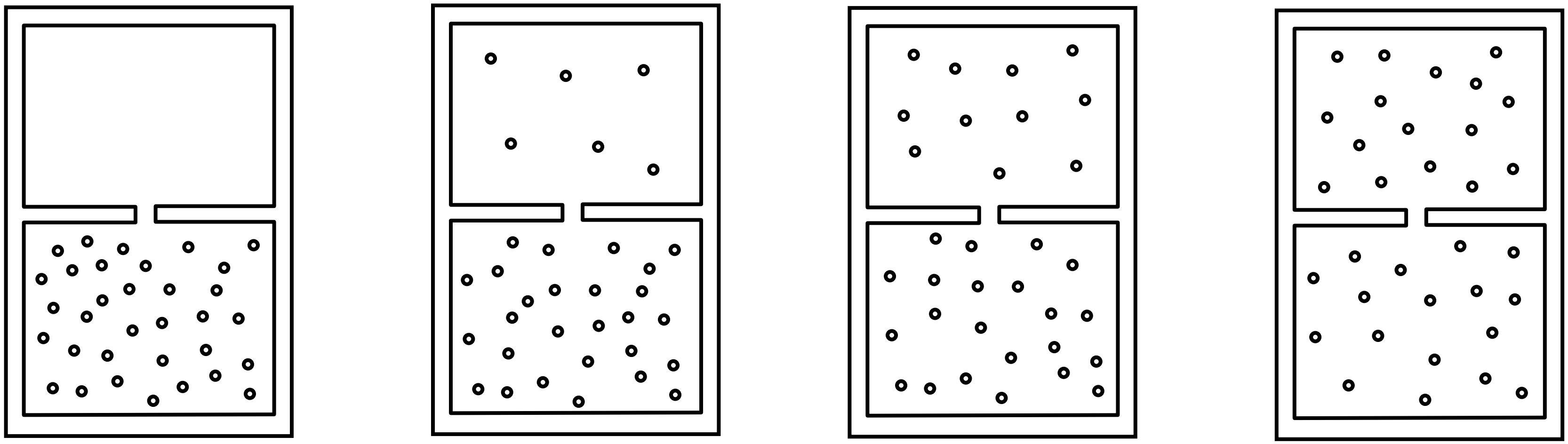


- All distributions $f(\mathbf{v}, t)$ are equally probable.
- <u>*But*</u>: There are many more uniform distributions than non-uniform ones.
- <u>*So*</u>: Choosing an initial state at random will in general lead to a uniform equilibrium state.

Boltzmann's Response, Part 2 (1877b)

"Über die Beziehung zwisschen dem zweiten Haubtsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeits-rechnung resp. dem Sätzen über das Wärmegleichgewicht"

- The transition from kinetic theory to statistical mechanics?
- Consider different "macrostates" of a gas:



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

- *Note:* Permuting any of the particles in a given macrostate with the same velocities doesn't change the macrostate.
- *Boltzmann's Intuition*: The equilibrium macrostate is the macrostate that has the maximum number of allowed permutations.

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

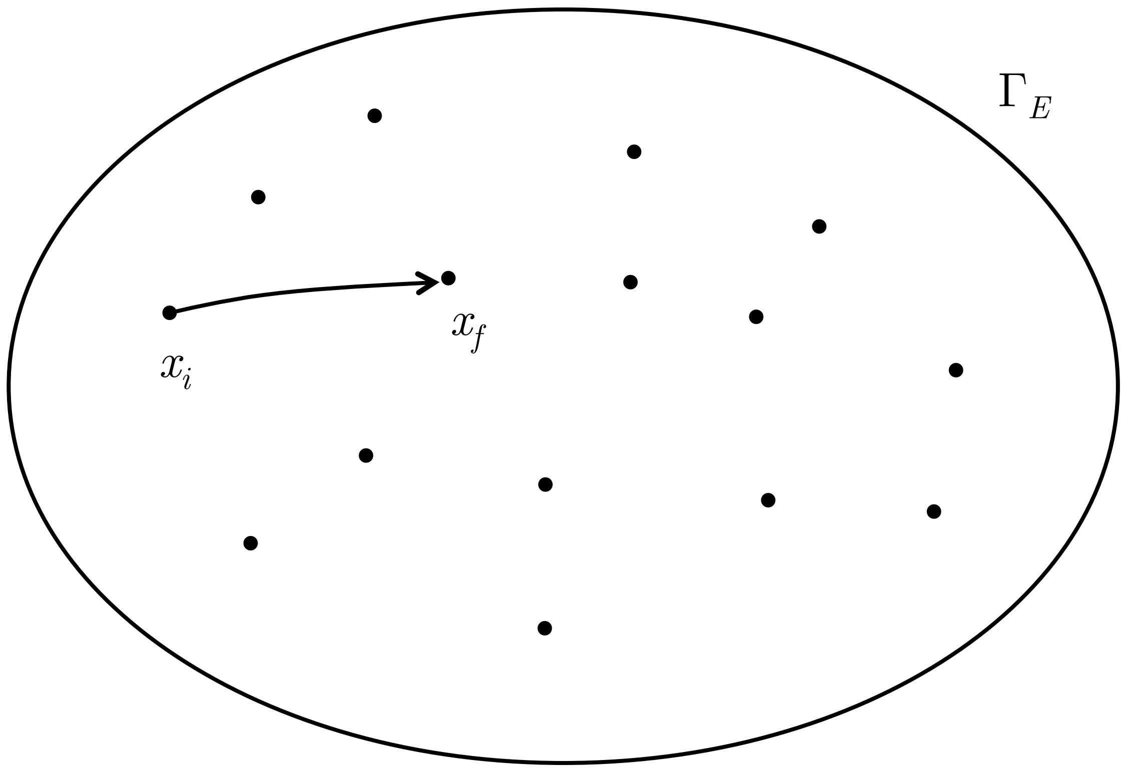
> A *microstate* ("*komplexion*") x of the gas is a specification of the position (3 values) and velocity (3 values) for each of its N particles.

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

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

Within Γ_E, Hamiltonian dynamics maps any initial microstate x_i to unique final microstate x_f.

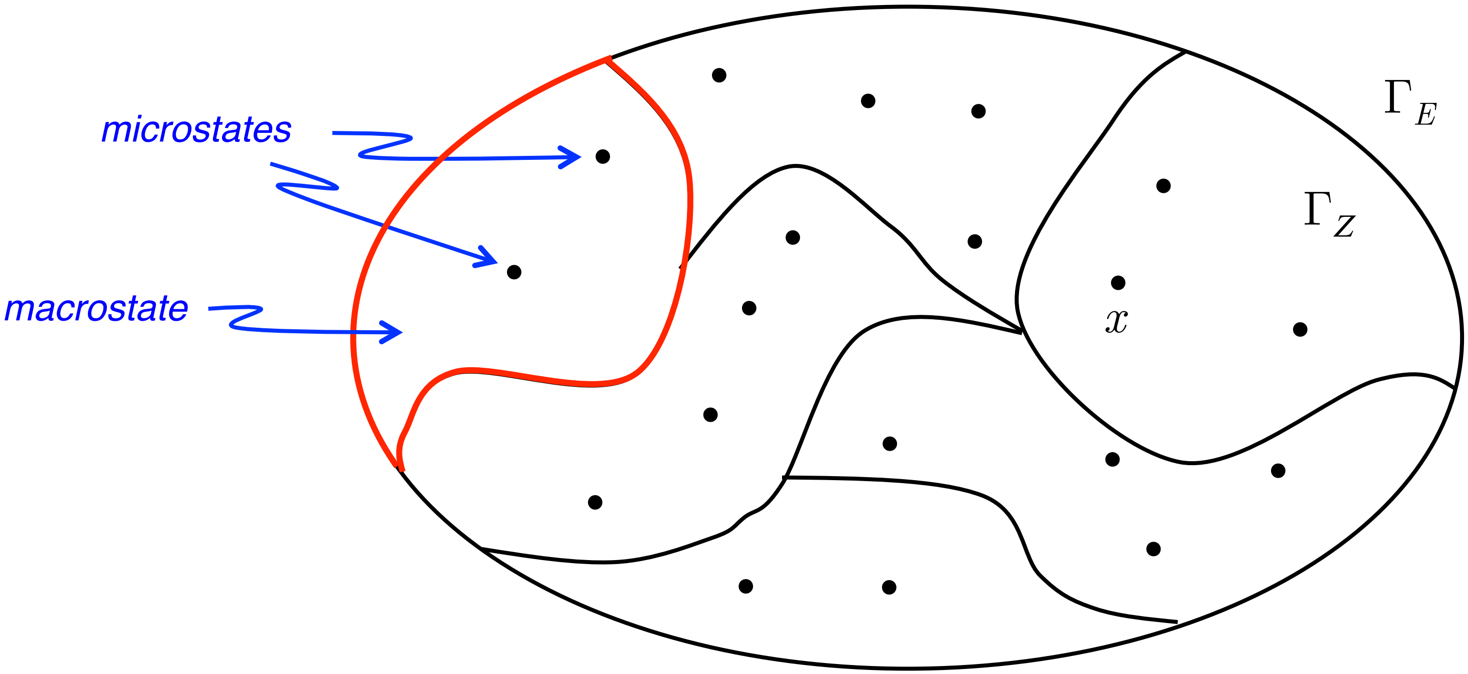
Can 2nd Law be explained by recourse to this dynamics?



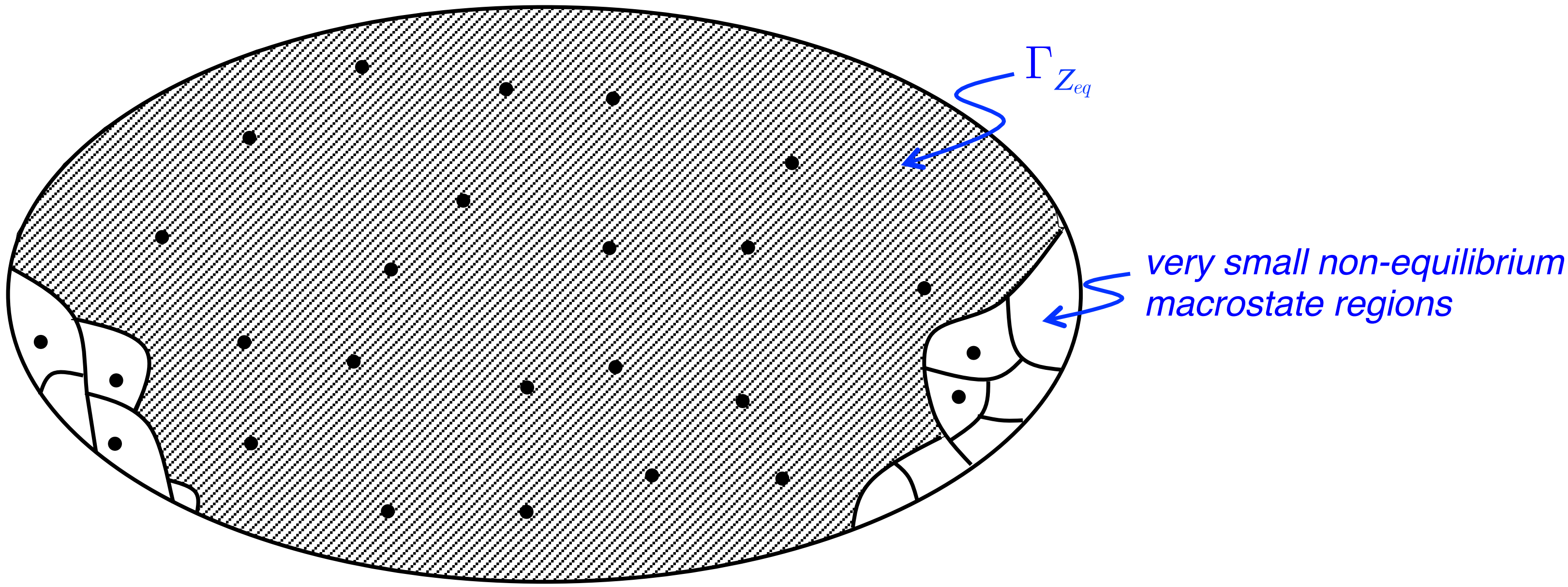
A *macrostate* Z of the gas (a "*state distribution*") is a specification of the gas in terms of macroscopic properties (pressure, temperature, volume, *etc.*).

- *To each microstate* x*, there corresponds exactly one macrostate* $Z(x)$.
- *Many distinct microstates* x, x', x'', ... *can correspond to the same macrostate:* $Z(x) = Z(x') = Z(x'') = ...$

- <u>*So*</u>: Γ_E is partitioned into a finite number of regions Γ_Z corresponding to macrostates, with each microstate x belonging to one region Γ_Z.



Boltzmann's Claim: The region $\Gamma_{Z_{eq}}$ corresponding to the equilibrium macrostate Z_{eq} is *vastly larger* than any other region, so it contains the vast majority of possible microstates.



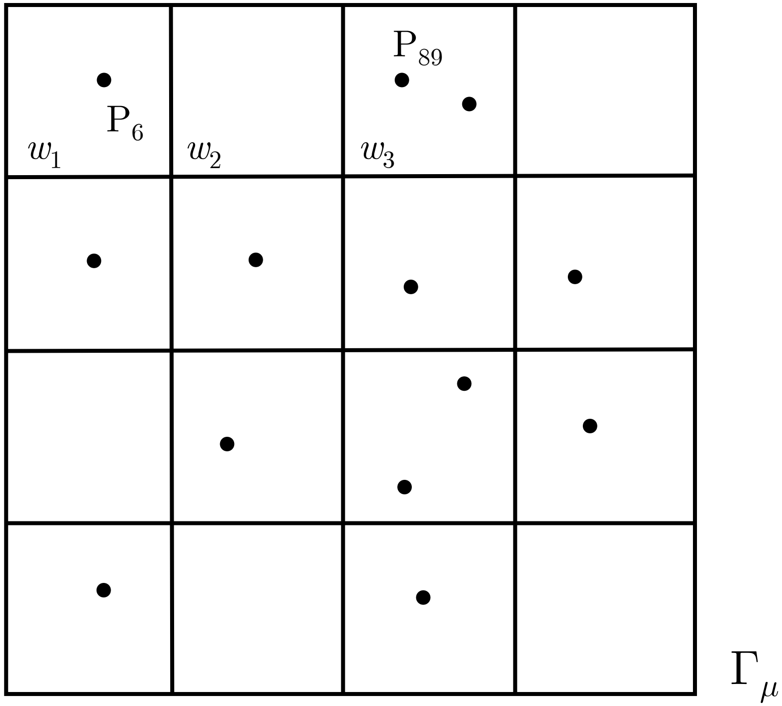
- *Thus*: For any initial microstate x_i, the dynamics will map x_i into $\Gamma_{Z_{eq}}$ very quickly, and then keep it there for an extremely long time.
- *Now*: How can we prove this?

- *Key Idea*: Associate probabilities with the size of macrostate regions: the larger the macrostate region, the greater the probability of finding a microstate in it.

- *Thus*:

> *A system approaches equilibrium because it evolves from macrostates of lower toward macrostates of higher probability, and the equilibrium macrostate is the macrostate of 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."



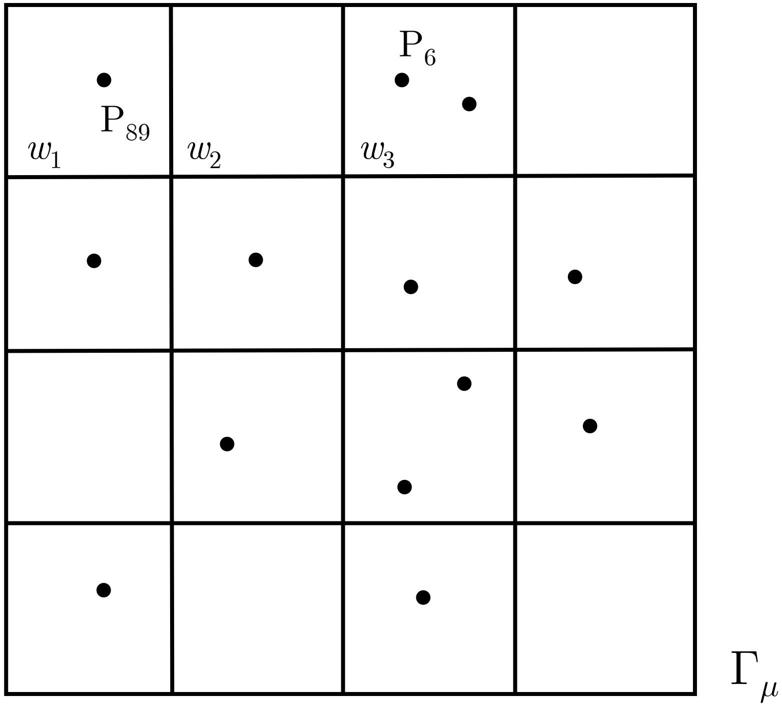
Arrangement #1:
state of P_6 in w_1, state of P_{89} in w_3, *etc.*

- Start with the *6-dim* phase space Γ_μ of a single particle.
- Partition Γ_μ into ℓ cells w_1, w_2, ..., w_ℓ of size $\Delta w = \Delta \mathbf{x} \Delta \mathbf{v}$.
- A state of an N-particle system is given by N points in Γ_μ.

Γ_E = N copies of Γ_μ

point in Γ_μ = single-particle microstate.

An *arrangement* is a specification of *which* points lie in which cells.



Arrangement #1:
state of P$_6$ in w_1, state of P$_{89}$ in w_3, *etc.*

Arrangement #2:
state of P$_{89}$ in w_1, state of P$_6$ in w_3, *etc.*

Macrostate:
(1, 0, 2, 0, 1, 1, ...)

Takes form $Z = (n_1, n_2, ..., n_\ell)$, where $n_j = \#$ of points in w_j.

- Start with the *6-dim* phase space Γ_μ of a single particle.
- Partition Γ_μ into ℓ cells $w_1, w_2, ..., w_\ell$ of size $\Delta w = \Delta \mathbf{x} \Delta \mathbf{v}$.
- A state of an N-particle system is given by N points in Γ_μ.

$\Gamma_E = N$ copies of Γ_μ

point in Γ_μ = single-particle microstate.

An *arrangement* is a specification of *which* points lie in which cells.

A *macrostate Z* is a specification of *how many* points (regardless of *which* ones) lie in each cell.

- *Note*: More than one arrangement can correspond to the same macrostate.

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

Answer: $$G(Z) = \frac{N!}{n_1!n_2!\cdots n_\ell!}$$

$$\begin{aligned} n! &= n(n-1)(n-2)\cdots 1 \\ &= \#\ \textit{of ways to arrange } n \textit{ distinguishable objects} \\ 0! &= 1 \end{aligned}$$

Check:

- Let $Z_1 = (N, 0, ..., 0)$ and $Z_2 = (N-1, 1, 0, ..., 0)$.
- $G(Z_1) = N!/N! = 1$. (Only one way for all N particles to be in w_1.)
- $G(Z_2) = N!/(N-1)! = N(N-1)(N-2)\cdots 1/(N-1)(N-2)\cdots 1 = N$.
  (There are N different ways w_2 could have one point in it; namely, if P_1 was in it, or if P_2 was in it, or if P_3 was in it, *etc*...)

- What is the size of the region Γ_Z corresponding to a macrostate Z?

- *Note*: The size of the region Γ_Z is given by the number of points it contains (*i.e.*, the number of arrangements compatible with Z) multiplied by a volume element of Γ_E.
- *And:* A volume element of Γ_E is given by N copies of a volume element Δw of Γ_μ.

- *Thus*: The size of Γ_Z is $|\Gamma_Z| = G(Z)\Delta w^N = \dfrac{N!}{n_1!n_2!\cdots n_\ell!}\Delta w^N$

- *Note*: $\ln|\Gamma_Z| = \ln\left(\frac{N!}{n_1!n_2!\cdots n_\ell!}\Delta w^N\right)$

$$= \ln N! - \ln n_1! - \ldots - \ln n_\ell! + N\ln\Delta w$$

$$\approx (N\ln N - N) - (n_1 \ln n_1 - n_1) - \ldots - (n_\ell \ln n_\ell - n_\ell) + N\ln\Delta w$$

$$= N\ln N - \sum_{i=1}^{\ell} n_i \ln n_i + N\ln\Delta w$$

Stirling's approx:
$\ln(n!) \approx n\log n - n$

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

- *Suppose*: $n_i = Nf(\mathbf{x}_i, \mathbf{v}_i)\Delta w = Nf(\mathbf{x}_i, \mathbf{v}_i)\Delta\mathbf{x}_i\Delta\mathbf{v}_i$

number of particles with position in range $\Delta\mathbf{x}_i$ and velocity in range $\Delta\mathbf{v}_\mathbf{i}$.

- *Then*: $\sum_i n_i \ln n_i = \sum_i Nf(\mathbf{x}_i, \mathbf{v}_i)\ln[Nf(\mathbf{x}_i, \mathbf{v}_i)\Delta w]\Delta\mathbf{x}_i\Delta\mathbf{v}_i$

$$\approx N\int f(\mathbf{x}, \mathbf{v})\Big(\ln f(\mathbf{x}, \mathbf{v}) + \ln N + \ln\Delta w]\Big)d\mathbf{x}\,d\mathbf{v}$$

$$= NH + N\ln N + N\ln\Delta w$$

- *So*: $\ln|\Gamma_Z| \approx -NH$
- *Now*: Define the "Boltzmann entropy" $S_B \equiv k\ln|\Gamma_Z|$, $k = \text{const}$.
- *Then*: $S_B \propto -H$.

$$S_B \equiv k\ln|\Gamma_Z|$$

A measure of the size of Γ_Z!

$$S_T = {}_R\int_i^f \frac{\delta Q_R}{T}$$

A measure of absolute changes in heat per temp of a reversible process!

What is the notion of probability?

- *Probability of macrostate = volume of macrostate region.*
- Earlier work (Maxwell 1860, 1866; Boltzman 1872): A distribution defines a probability measure over the states of gas particles.
  - *Probabilities are assigned to the states of gas particles.*
- Boltzmann (1877b): A distribution (macrostate), instead of defining a probability, is now assigned a probability.
  - *Probabilities are not assigned to particle states, but to the state of the gas as a whole.*

How is this a response to Loschmidt's objection?

- *Boltzmann says*: Any initial microstate x_i will evolve under Hamiltonian dynamics to a region with greater probability (as measured by its size).
- *But*: *Nothing* in Hamiltonian dynamics entails that states associated with low probabilities evolve into states associated with high probabilities.
  - *Ex: Any state in Γ_E cannot evolve into a region, no matter how large, outside Γ_E (conservation of energy).*

2. Poincaré's Recurrence Theorem (1890).

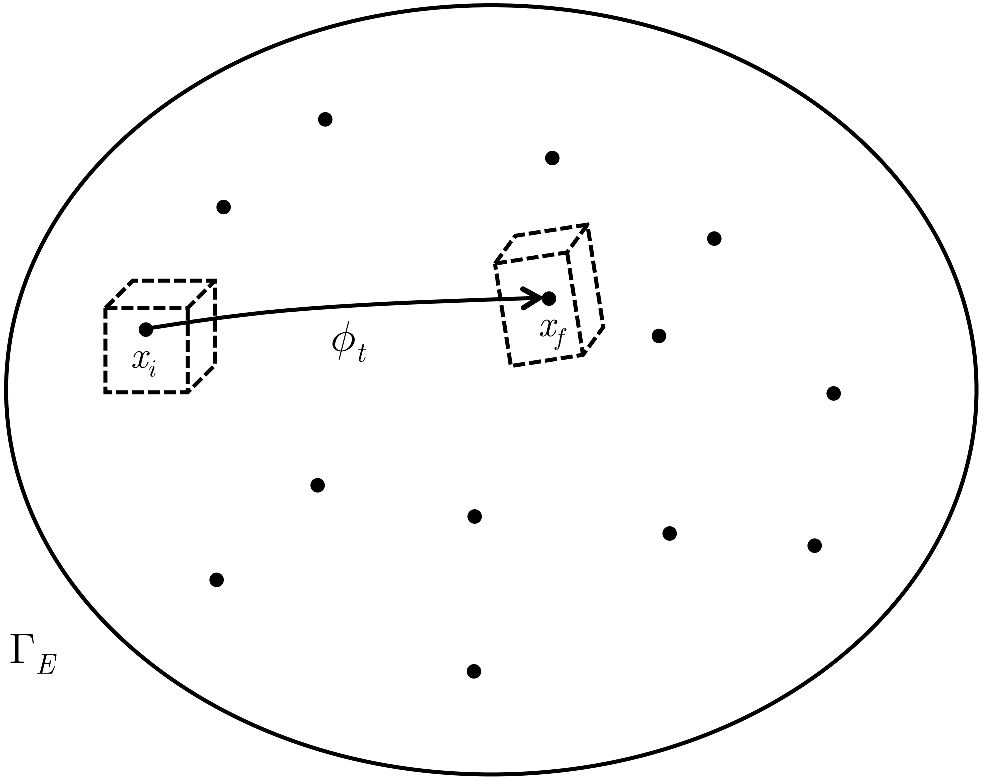
"On the 3-body Problem and the Equations of Dynamics"

Henri Poincaré
(1854-1912)

> *Theorem*: For every *mechanical* system with a bounded phase space, *almost every* initial state of the system will, after some finite time, return to a state arbitrarily close to the initial state.

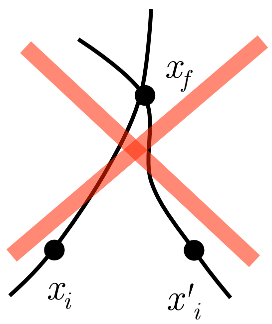
- *Consider*: Gas consisting of N particles governed by Hamilton's equations of motion.
- *Recall*: A *microstate* of the gas is a specification of the position (3 values) and velocity (3 values) for each of its N particles.

  - Γ = *phase space* = $6N$-dim space of all possible microstates.
  - Γ_E = region of Γ that consists of all microstates with constant energy E.
  - Hamilton's equations define a map $\phi_t : \Gamma \to \Gamma$ that maps any initial state x_i in Γ_E to a *unique* final state x_f in Γ_E.
  - *Key property*: ϕ_t preserves volumes.



Aside: Informal Proof.

- *We know*: Trajectories in phase space do not intersect (because ϕ_t is *deterministic*: any given state cannot have evolved from two separate initial states).
- *And*: Phase space volumes are preserved by ϕ_t.
- *So*: A tube swept out by ϕ_t from an initial region A can never cross regions it has already crossed.
- *And*: Assuming phase space is finite and ϕ_t preserves volumes, at some point, all of phase space will be swept out.
- *Thus*: In order to continue evolving, the tube must connect back to A (otherwise it would intersect a region it's already crossed).



"A theorem, easy to prove, tells us that a bounded world, governed only by the laws of mechanics, will always pass through a state very close to its initial state. On the other hand, according to accepted experimental laws (if one attributes absolute validity to them, and if one is willing to press their consequences to the extreme), the universe tends toward a certain final state, from which it will never depart. In this final state, which will be a kind of death, all bodies will be at rest at the same temperature."

"I do not know if it has been remarked that the English kinetic theories can extricate themselves from this contradiction. The world, according to them, tends at first toward a state where it remains for a long time without apparent change; and this is consistent with experience; but it does not remain that way forever, if the theorem cited above is not violated; it merely stays there for an enormously long time, a time which is longer the more numerous are the molecules. This state will not be the final death of the universe, but a sort of slumber, from which it will awake after millions of millions of centuries. According to this theory, to see heat pass from a cold body to a warm one, it will not be necessary to have the acute vision, the intelligence, and the dexterity of Maxwell's demon; it will suffice to have a little patience."

- Poincare (1893) "Le mécanisme et l'expérience".

3. Zermelo's *Wiederkehreinwand* (Recurrence Objection) (1896).

"On a Theorem of Dynamics and the Mechanical Theory of Heat"

Ernst Zermelo
(1871-1953)

"Poincaré's theorem says that *in a system of mass-points under the influence of forces that depend only on position in space* [*i.e.*, a conserved Hamiltonian system], *in general any state of motion (characterized by configurations and velocities) must recur arbitrarily often, at least to any arbitrary degree of approximation even if not exactly, provided that the coordinates and velocities cannot increase to infinite* [*i.e.*, the phase space is bounded]."

"Hence, in such a system *irreversible processes are impossible* since (aside from singular initial states) no single-valued continuous function of the state variables, such as entropy, can continually increase; if there is a finite increase, then there must be a corresponding decrease when the initial state recurs."

- <u>*In other words*</u>: For any continuous function $F(x)$ on phase space, $F(\phi_t x)$ cannot be monotonically increasing in time (except for when the initial state x is a singular state).
- <u>*So*</u>: The H-Theorem is incompatible with the underlying mechanical laws of motion.

Options

(1) Drop assumption that phase space is bounded: allow infinite velocities or infinite distances. *But*: Not realistic for gases.

(2) Drop assumption that dynamics is Hamiltonian. *But*: Physical systems obey Hamilton's equations.

(3) Assume only singular states exist (states in regions with measure zero).

"...in order to establish the general validity of the second law of thermodynamics, one would have to assume that only those initial states that lead to irreversible processes are actually realized in nature, despite their smaller number, while the other states, which from a mathematical viewpoint are more probable, actually *do not occur*."

- *But*: Overwhelming majority of possible states are *not* singular; why should Nature only realize singular states?
- *And*: Smallest change in variables can change a singular state into a recurring state.

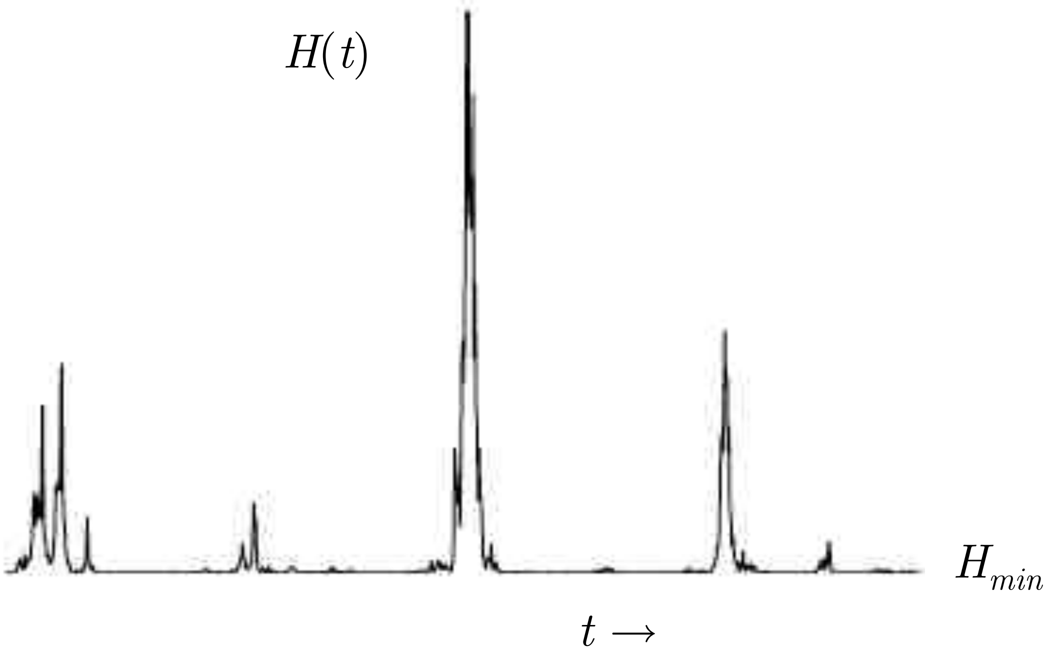
"[This assumption would be]... quite unique in physics and I do not believe that anyone would be satisfied with it for very long."

"It is now necessary to formulate either the Carnot-Clausius principle or the mechanical theory in an essentially different way, or else decide to give up the latter theory altogether."

Boltzmann's Response, Part 1 (1896)

"Rely to Zermelo's Remarks on the Theory of Heat"

- *Consider*: "H-curve" for a gas in a container with finite particles and $t \to \infty$, for any "non-singular" initial state:



- $H(t)$ is usually very close to H_{min} (Maxwell equilibrium distribution).
- Fluctuations away from H_{min} are rare.
- Probability of a fluctuation decreases with its height.
- *So*: Given a non-singular initial microstate far from equilibrium, at any later time it should have evolved into a microstate very close to equilibrium.

"Rely to Zermelo's Remarks on the Theory of Heat"

Boltzmann's Response, Part 1 (1896)

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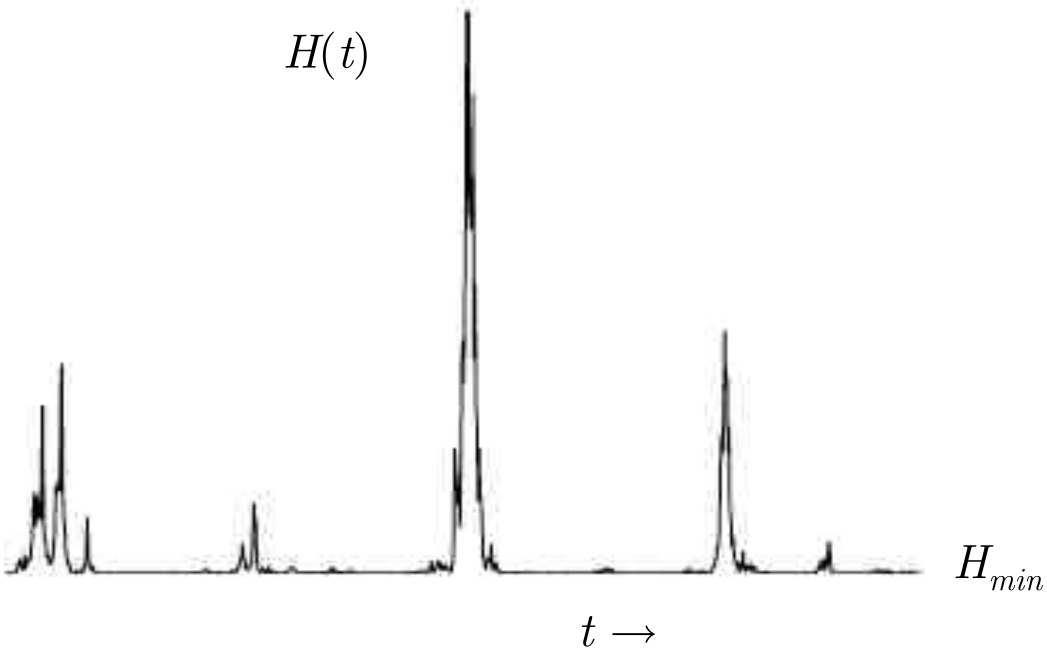
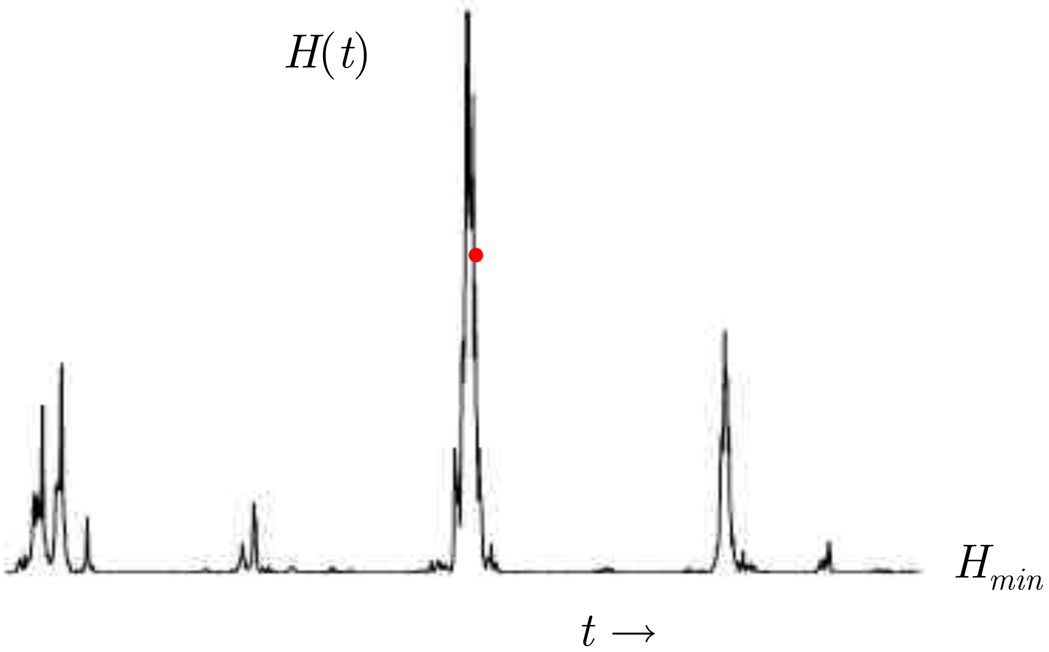


"Zermelo thinks that he can conclude from Poincaré's theorem that it is only for certain singular initial states, whose number is infinitesimal compared to all possible initial states, that the Maxwell distribution will be approached, while for most initial states this law is not obeyed. This seems to me to be incorrect. It is just for certain singular initial states that the Maxwell distribution is never reached, for example when all the molecules are initially moving in a line perpendicular to two sides of the container. For the overwhelming majority of initial conditions, on the other hand, the *H*-curve has the character mentioned above."

Boltzmann's Response, Part 1 (1896)

- *Consider*: "H-curve" for a gas in a container with finite particles and $t \to \infty$, for any "non-singular" initial state:

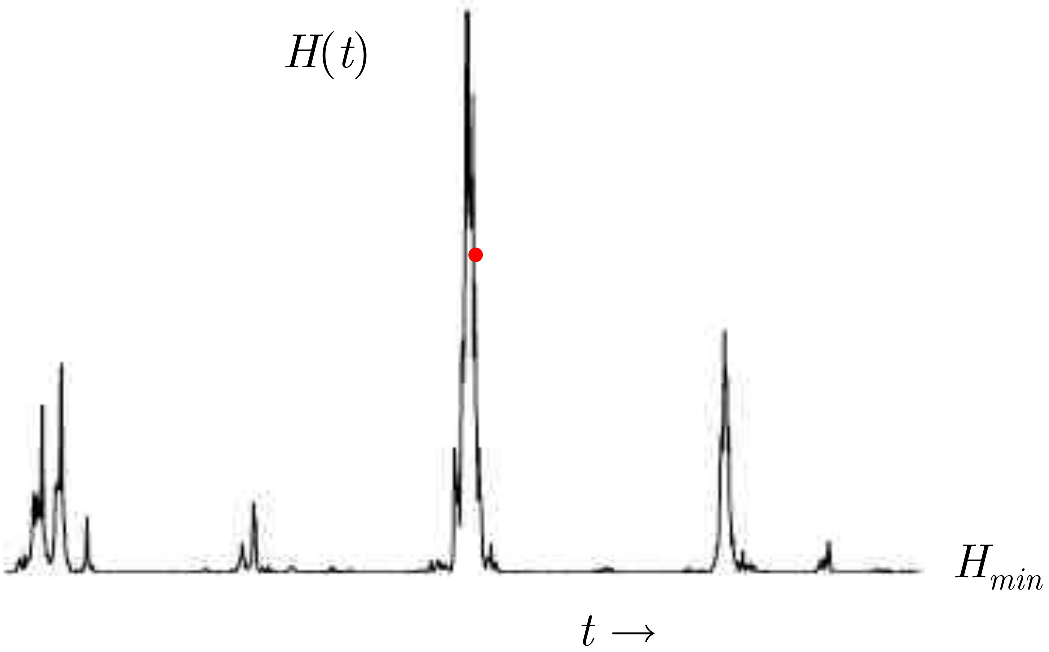


"If the initial state lies on an enormously high peak, *i.e.* if it is completely different from the Maxwellian state, then the state will approach this velocity distribution with enormously large probability, and during an enormously long time it will deviate from it by only vanishingly small amounts. Of course if one waits an even longer time, he may observe an even higher peak, and indeed the initial state will eventually recur; in a mathematical sense one must have an infinite time duration infinitely often. Zermelo is therefore completely correct when he asserts that the motion is periodic in a mathematical sense; but, far from contradicting my theorem, this periodicity is in complete harmony with it."

Boltzmann's Response, Part 1 (1896)

"Rely to Zermelo's Remarks on the Theory of Heat"

- *Consider*: "H-curve" for a gas in a container with finite particles and $t \to \infty$, for any "non-singular" initial state:

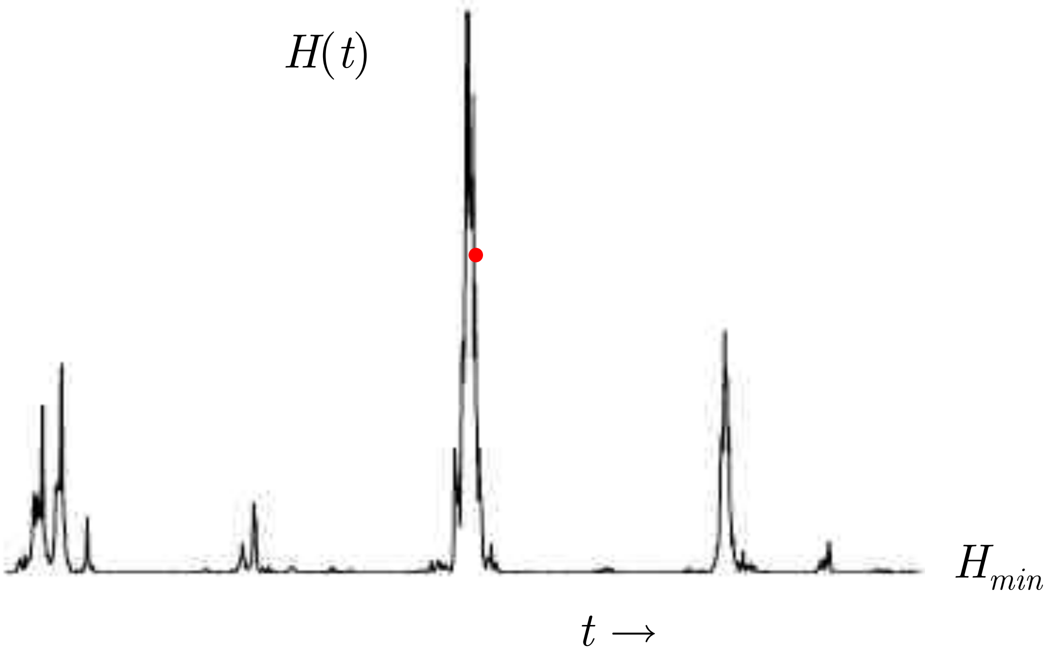


"We therefore arrive at the following result: if one considers heat to be molecular motion which takes place according to the general equations of mechanics, and assumes that the complexes of bodies that we observe are at present in very improbable states, then one can obtain a theorem which agrees with the second law for phenomena observed up to now."

<u>*Zermelo's Counter-Response (1896)*</u>

"On the Mechanical Explanation of Irreversible Processess."

- <u>*Consider*</u>: "H-curve" for a gas in a container with finite particles and $t \to \infty$, for any "non-singular" initial state:

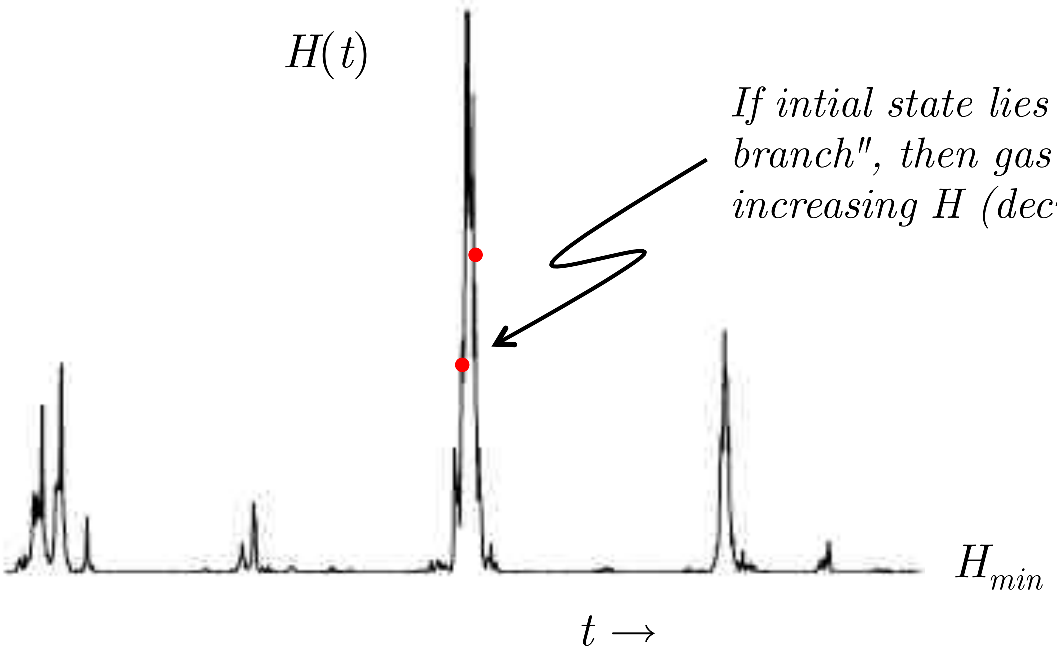


"It is not sufficient to show that all perturbations finally relax to a long-lasting equilibrium state; rather it is necessary to show that changes always take place in the same sense, in the direction of equalization; that the H-function *always only* decreases during observable times, or at least that there can only be very small, practically unnoticeable increases, which will always be immediately washed out by stronger decreases."

Zermelo's Counter-Response (1896)

"On the Mechanical Explanation of Irreversible Processess."

- *Consider*: "H-curve" for a gas in a container with finite particles and $t \to \infty$, for any "non-singular" initial state:



"In my opinion this proof is as little possible for the H-function as for any other function. Clearly the initial state, whose probability can depend only on the initial value H_0, can just as well lie on a rising as a falling branch of the curve, and in the former case there must first be an *increase*, which can last just as long as the subsequent decrease."

Boltzmann's Response, Part 2 (1897)

"On Zermelo's Paper 'On the Mechanical Explanation of Irreversible Processes."

- Why does the initial state of a system lie on a maximum of the H-curve (or just past the maximum)?

"[Suppose] the universe considered as a mechanical system -- or at least a very large part of it which surrounds us -- started from a very improbable state, and is still in an improbable state. Hence if one takes a smaller system of bodies in the state in which he actually finds them, and suddenly isolates this system from the rest of the world, then the system will initially be in an improbable state, and as long as the system remains isolated it will always proceed toward more probable states."

- *The Past Hypothesis*: The initial macrostate of the universe was a macrostate with a large H-value (*i.e.*, low entropy).
- *Idea*: No states before initial state of universe.
- *But*: Just because the entropy of the global macrostate of the universe increases doesn't imply that the entropy of the macrostate of a small subsystem increases, too.
- *Moreover*:

"[This hypothesis]... is, of course, unprovable."

"On the other hand, if we do not make any assumption about the present state of the universe, then of course we cannot expect to find that a system isolated from the universe, whose initial state is completely arbitrary, will be in an improbable state initially rather than later. On the contrary it is to be expected that at the moment of separation the system will be in thermal equilibrium. In the few cases where this does not happen, it will almost always be found that if the state of the isolated system is followed either backwards or forwards in time, it will almost immediately pass to a more probable state. Much rarer will be the cases in which the state becomes still more improbable as time goes on; but such cases will be just as frequent as those where the state becomes more improbable as one follows it backwards in time."

- So: If we don't adopt the Past Hypothesis, then four options for the initial state of an isolated system:

(i) *Most probable*: thermal equilibrium.

(ii) *Less probable*: non-equilibrium at an H-curve maximum. H thus decreases in both directions of time.

(iii) *Even less probable*: non-equilibrium on an increasing flank of H-curve.

(iv) *Equally probable as (iii)*: non-equilibrium on a decreasing flank of H-curve.

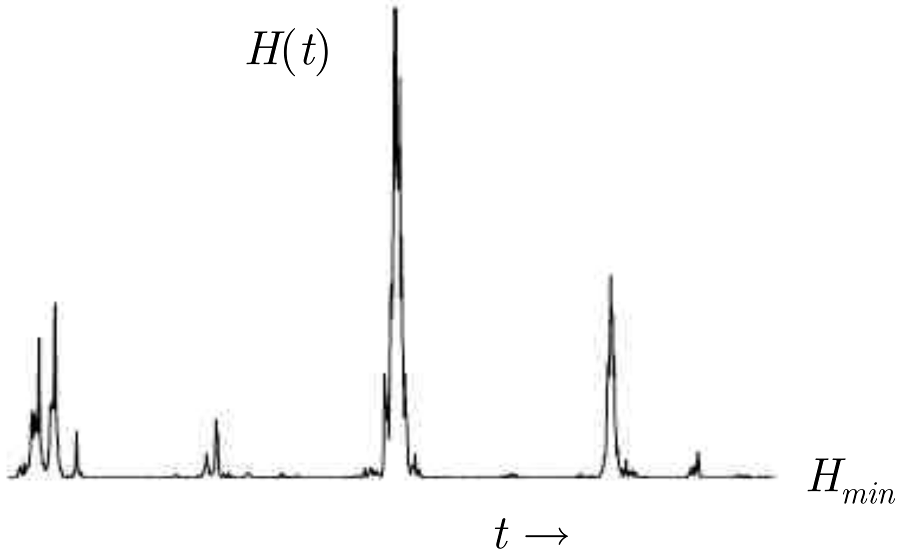
Possible initial states of isolated systems:

(i) *Most probable*: thermal equilibrium.

(ii) *Less probable*: non-equilibrium at an H-curve maximum. H thus decreases in both directions of time.

(iii) *Even less probable*: non-equilibrium on an increasing flank of H-curve.

(iv) *Equally probable as (iii)*: non-equilibrium on a decreasing flank of H-curve.



- We don't typically observe (i).
- (ii) is problematic: Value of H in 1896 should be *increasing* as time decreases.
- Can (iii) and (iv) be defended?

"One has the choice of two kinds of pictures. One can assume that the entire universe finds itself at present in a very improbable state. However, one may suppose that the eons during which this improbable state lasts, and the distance from here to Sirius, are minute compared to the age and size of the universe. There must then be in the universe, which is in thermal equilibrium as a whole and therefore dead, here and there relatively small regions of the size of our galaxy (which we call worlds), which during the relatively short time of eons deviate significantly from thermal equilibrium. Among these worlds the state probability increases as often as it decreases. For the universe as a whole the two directions of time are indistinguishable, just as in space there is no up or down. However, just as at a certain place on the earth's surface we can call 'down' the direction toward the centre of the earth, so a living being that finds itself in such a world at a certain period of time can define the time direction as going from less probable to more probable states (the former will be the 'past' and the latter the 'future') and by virtue of this definition he will find that this small region, isolated from the rest of the universe, is 'initially' always in an improbable state."

- The universe is presently in a global "dead" state of thermal equilibrium with regions of non-equilibrium that support life.
  - *Most probable state of universe is equilibrium.*
  - *<u>But</u>: The universe is big, so the probability of a relatively small region being in any state (including an improbable non-equilibrium state) can be as large as we please.*
- *<u>Anthropic Principle</u>*: We find ourselves in a region of non-equilibrium, since non-equilibrium is essential for the existence of living beings.

"One has the choice of two kinds of pictures. One can assume that the entire universe finds itself at present in a very improbable state. However, one may suppose that the eons during which this improbable state lasts, and the distance from here to Sirius, are minute compared to the age and size of the universe. There must then be in the universe, which is in thermal equilibrium as a whole and therefore dead, here and there relatively small regions of the size of our galaxy (which we call worlds), which during the relatively short time of eons deviate significantly from thermal equilibrium. Among these worlds the state probability increases as often as it decreases. For the universe as a whole the two directions of time are indistinguishable, just as in space there is no up or down. However, just as at a certain place on the earth's surface we can call 'down' the direction toward the centre of the earth, so a living being that finds itself in such a world at a certain period of time can define the time direction as going from less probable to more probable states (the former will be the 'past' and the latter the 'future') and by virtue of this definition he will find that this small region, isolated from the rest of the universe, is 'initially' always in an improbable state."

- In regions of non-equilibrium, H increases as often as it decreases (cases (iii) and (iv)).
- *But*: The direction of time is just the direction in which one goes from less to more probable states.
- *So*: Cases (iii) and (iv) are indistinguishable: both involve H decreasing (and thus entropy increasing) as time increases.

"The combination of cosmological speculation, transendental deduction, and definitional dissolution in these short remarks has been credited by many as one of the most ingenious proposals in the history of science, and disparaged by others as the last patently desperate, *ad hoc* attempt to save an obviously failed theory." (Sklar 1993, pg. 44.)