

The Second Law, Boltzmann's Entropy and Typical Behavior of Macroscopic Systems

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For Giovanni with affection

Abstract

In this talk I will try to illustrate, via some examples, Boltzmann's ideas about the relation between the microscopic time reversible dynamics and macroscopic irreversibility. These can be summarized as follows: Time-asymmetric behavior, as embedded in the second law of thermodynamics, is observed in individual macroscopic systems. It can be understood as arising naturally from time symmetric microscopic laws when account is taken of a) the great disparity between microscopic and macroscopic sizes, b) initial conditions, and c) what we observe are typical behaviors-not all imaginable ones. While Boltzmann considered classical microscopic laws his conclusions also hold, with some modifications, for quantum systems.

Introduction

My summary of Boltzmann's ideas above is far from original. They are in fact just what Einstein wrote in his tribute to Boltzmann:

*“On the basis of kinetic theory of gases Boltzmann had discovered that, aside from a constant factor, entropy is equivalent to the logarithm of the “probability” of the [macroscopic] state under consideration. Through this insight he recognized the nature of course of events which, in the sense of thermodynamics, are “irreversible”. Seen from the molecular-mechanical point of view, however all courses of events are reversible. If one calls a molecular-theoretically defined state a microscopically described one, or, more briefly, micro-state, then an immensely large number (Z) of states belong to a macroscopic condition. Z is then a measure of the probability of a chosen macro-state. **This idea appears to be of outstanding importance also because of the fact that its usefulness is not limited to microscopic description on the basis of mechanics.**” — A. Einstein, Autobiographical notes*

The great insight of Boltzmann was, as Einstein says, to identify the entropy of a macroscopic system in a specified macrostate with the logarithm of the “number”, something proportional to phase space volume, of the microstates corresponding to that macrostate. He did this not only for the case where the macrostate is an equilibrium state for which the thermodynamic entropy was specified by Clausius but also for nonequilibrium macrostates.

To quote Boltzmann¹ in connection with his eponymous equation for dilute gases:

“In one respect we have even generalized the entropy principle here, in that we have been able to define the entropy in a gas that is not in a stationary [equilibrium] state.”

¹Bo98

The rest of my talk will be an elaboration of this theme for classical and quantum systems. I will do that using the formalism of the usual microcanonical ensemble or those derived from it by constraining the microstates to regions corresponding to nonequilibrium macrostates.

These take “probability” to be proportional to phase space volume in classical systems and to “number of independent wave functions” in quantum systems.

Classical Systems

In classical mechanics, the microstate of an isolated system of N particles confined to a box V in \mathbb{R}^d is a point X in the $2dN$ -dimensional phase space, Γ ,

$$X = (\mathbf{r}_1, \mathbf{v}_1, \dots, \mathbf{r}_N, \mathbf{v}_N), \quad \mathbf{r}_i \in V \subset \mathbb{R}^d, \quad \mathbf{v}_i \in \mathbb{R}^d \quad (1)$$

Its time evolution is given by a Hamiltonian $H(X)$ which conserves energy, so $X(t) = T_t X$ will be confined to the energy surface $H(X) = E$. We can take $H(X)$ to be of the form

$$H(X) = \frac{1}{2} \sum_{j=1}^N v_j^2 + \sum_{i < j} u(r_{i,j}) \quad (2)$$

with rapidly decaying $u(r)$.

Macrostates

To describe the macroscopic state of such a system we make use of a much cruder specification than that provided by the microstate X . We shall denote by M such a macroscopic description.

In general we can specify the macrostate of a system by giving an n -tuple of macrovariables $M(X) = \{M_1(X), M_2(X), \dots, M_n(X)\}$, with resolution $\Delta M = \{\Delta M_j\}$. The macrostates then correspond to the elements of the partition of the phase space into sets Γ_M of the form

$$\Gamma_M = \{X | M_j \leq M_j(X) \leq M_j + \Delta M_j, j = 1, \dots, n\}.$$

In particular we always choose one of these macro-variables to be the Hamiltonian and replace the energy surface by a thin shell surrounding that surface to which I shall always refer as Γ_E . We then have $\Gamma_M \subset \Gamma_E$.

It can be shown² that for all reasonable choices³ of the M 's there is in every Γ_E of a macroscopic system one dominant region Γ_M which has most of the volume of Γ_E . This is called the equilibrium macrostate M_{eq} ,

$$\frac{|\Gamma_{M_{\text{eq}}}|}{|\Gamma_E|} = 1 - \varepsilon \quad (3)$$

with $\varepsilon \ll 1$, and $|\Gamma_M|$ the Liouville volume of Γ_M .

A system in a microstate X is then in macroscopic thermal equilibrium relative to the choice of the M 's iff $X \in \Gamma_{M_{\text{eq}}}$. When M specifies a nonequilibrium state, $|\Gamma_M|$ is very much smaller than $|\Gamma_{M_{\text{eq}}}|$. The existence of a macrostate satisfying (3) is essentially a consequence of the law of large numbers.

²La73

³e.g. dividing up the box V into small regions and specifying, with some tolerances, the particle, momentum and energy densities in each region

All functions specifying **macroscopic** properties, not just those used to define the M 's, have approximately the same value for almost all $X \in \Gamma_{M_{\text{eq}}}$; hence these values are typical for the uniform measure on $\Gamma_{M_{\text{eq}}}$ and observed for (almost) all systems in equilibrium.

In fact since $|\Gamma_{M_{\text{eq}}}| \simeq |\Gamma_E|$ they are also typical of the microcanonical measure on Γ_E .

This is why one can use the microcanonical ensemble for $N \gg 1$ to compute macroscopic properties of an equilibrium system, independent of whether or not the dynamics is ergodic in a mathematical sense.

Approach to Equilibrium

Boltzmann (also Maxwell, Kelvin, ...) argued that given the disparity in the sizes of the Γ_M corresponding to the various macrostates, the evolution of the vast majority of microstates $X(t_0)$ in Γ_M , will for $N \gg 1$ be such that $|\Gamma_{M(X(t))}|$ will not decrease (on a macroscopic scale) for $t > t_0$ (and smaller than the Poincaré recurrence time which is larger than the age of the universe).

Thus the evolution towards equilibrium of macroscopic systems which start in the region Γ_M , $M \neq M_{\text{eq}}$, and are kept (effectively) isolated afterwards, is typical with respect to the micro-canonical measure restricted to Γ_M .

N.B. We have assumed that such measures give the right probabilities for physical systems.

Boltzmann's Entropy

To make a connection with the Second Law, Boltzmann identified the (Boltzmann) entropy of a macroscopic system in a microstate X as

$$S_B(X) = \log |\Gamma_{M(X)}| = S_B(M(X)) \quad (4)$$

up to a constant.

The entropy of the equilibrium macrostate is then given by

$$S_B(M_{\text{eq}}) = \log |\Gamma_{M_{\text{eq}}}| \simeq \log |\Gamma_E| \quad (5)$$

Boltzmann then showed that $S_B(M_{\text{eq}})$ agrees with the Clausius thermodynamic entropy of a gas in equilibrium.

Boltzmann's heuristic argument for the non-decrease of entropy, based on relative phase space volume, is the correct explanation for the behavior typically observed in actual macroscopic systems. It is, however, very far from a mathematical theorem and contains no quantitative information about time scales⁴.

A proof would be provided by the rigorous derivation from the microscopic dynamics of the kinetic and hydrodynamic equations⁵ commonly used to describe the time asymmetric, entropy increasing behavior of macroscopic systems out of equilibrium.

This has been achieved so far only for the Boltzmann equation for dilute gases. This was done rigorously (in appropriate limits) by Oscar Lanford in 1975.

⁴As Mark Kac said: an argument convinces a reasonable person, a proof convinces a stubborn one.

⁵such as the heat equation, Navier-Stokes equations, etc.

The Boltzmann Equation for Dilute Gases

We note that for a system of N particles in a box V that the microstate $X = \{\mathbf{r}_i, \mathbf{v}_i\}$, $i = 1, \dots, N$, can be considered as a set of N points in six dimensional one particle space.

Dividing up this one particle space into cells Δ_α , $\alpha = 1, \dots, n$, centered on $(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$, of volume $|\Delta_\alpha|$, we can describe the macro (meso) states of a gas M_f by specifying, with some leeway, that the fraction of particles $N_\alpha(X)/N$ in each Δ_α satisfy

$$f_\alpha |\Delta_\alpha| = N_\alpha/N \cong \int_{\Delta_\alpha} f(\mathbf{x}, \mathbf{v}) d\mathbf{x} d\mathbf{v}. \quad (6)$$

where $f(\mathbf{x}, \mathbf{v}) \geq 0$ is a smooth distribution in the one particle space. For a dilute gas with negligible potential energy, f specifies E , $\Gamma_{M_f} \subset \Gamma_E$. (When the potential energy is not negligible f does not specify the energy and we need to add the value of the energy to describe the macrostate, c.f. Goldstein-Lebowitz (2004).)

The Boltzmann entropy of a dilute gas in a macrostate M_f ,

$$S_B(f) = S_B(M_f) = \log |\Gamma_{M_f}| \quad (7)$$

was computed by Boltzmann: $|\Gamma_{M_f}| = \prod_{\alpha} |\Delta_{\alpha}|^{N_{\alpha}} / N_{\alpha}!$, so that for $N \gg 1$,

$$\frac{1}{N} S_B(f) = - \sum |\Delta_{\alpha}| f_{\alpha} \log f_{\alpha} + \text{const} \quad (8)$$

When $|\Delta_{\alpha}|$ is small we can, following Boltzmann, approximate (8) by

$$s_{\text{gas}}(f) \cong - \int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} f(\mathbf{x}, \mathbf{v}) \log f(\mathbf{x}, \mathbf{v}) + \text{const}. \quad (9)$$

While (9) looks like, and is sometimes mistakenly confused with the Gibbs-Shannon entropy per particle for in a product measure of the form $\prod_i f(\mathbf{x}_i, \mathbf{v}_i)$, it is conceptually not the same at all: $s_{\text{gas}}(f)$ is the entropy of an individual system with empirical distribution approximately $f(\mathbf{x}, \mathbf{v})$.

The maximum of $s_{\text{gas}}(f)$ over all f for a system of N particles in a volume $|V|$ with a given energy, which is for a dilute gas just the kinetic energy, is proportional to the Maxwell distribution

$$f_{\text{eq}} = \rho(2\pi kT/m)^{-3/2} \exp[-m\mathbf{v}^2/2kT] \quad (10)$$

where $kT = 2/3(E/N)$, $\rho = N/V$.

In this case $\Gamma_{M_{f_{\text{eq}}}} = \Gamma_{M_{\text{eq}}}$ and the entropy per particle is then given by

$$s_{\text{gas}}(f) = \frac{3}{2} \log T - \log \rho + \text{Const.} \quad (11)$$

the same as the equilibrium Clausius entropy per particle for a dilute gas, with density ρ .

Lanford's Theorem

Consider a gas consisting of N spheres of diameter d in a volume $V \subset \mathbb{R}^3$ evolving according to Hamiltonian dynamics with elastic collisions, in the macrostate M_{f_0}

Keeping V fixed consider now a sequence of systems with different particle numbers, and different diameters d , such that $N \rightarrow \infty$, $d \rightarrow 0$, while $Nd^2 \rightarrow b > 0$ (and so $Nd^3 \rightarrow 0$). This is called the Boltzmann-Grad (BG) limit. b^{-1} is proportional to the mean-free-path between collisions.

As N increases the fraction of particles in cubical boxes Δ_α is required to satisfy (6) ever more closely, with equality in the BG limit,

$$\lim_{\text{BG}} N_\alpha(X_N)/N = \int_{\Delta_\alpha} f_0(\mathbf{x}, \mathbf{v}) d\mathbf{x}d\mathbf{v}. \quad (12)$$

N.B. The BG limit is required for (12) to hold for arbitrarily small Δ_α . The exact distribution of a finite system of N particles is a sum of N delta functions, not a smooth f .

Lanford's theorem then says (roughly):

Given f_0 , a microstate $X_N(0) \in \Gamma_{M_{f_0}}$ will, typically evolve, via the Hamiltonian dynamics, to a microstate $X_N(t)$ such that, for sufficiently large N ,

$$\frac{N_\alpha(X_N(t))}{N} \cong \int_{\Delta_\alpha} f(\mathbf{x}, \mathbf{v}, t) d\mathbf{x}d\mathbf{v} \quad (13)$$

where $f(\mathbf{x}, \mathbf{v}, t)$ solves the well-known Boltzmann equation

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{x}} = bQ(f, f) \quad (14)$$

with initial condition $f_0(\mathbf{x}, \mathbf{v})$. Eq (13) becomes exact in the BG limit.

The BE gives a deterministic evolution from the macrostate M_{f_0} to M_{f_t} in the BG limit. It will hold to a good approximation for a macroscopic dilute gas. It accurately describes the typical time evolution of the “empirical” distribution of atoms in the one particle space of such an individual system induced by collisions.

The second law now says that for a *typical* microstate of a dilute gas with $X(0) \in \Gamma_{M_{f_0}}$, $X(t) = T_t X(0) \in \Gamma_{M_{f_t}}$, $s_{\text{gas}}(f_t) \geq s_{\text{gas}}(f_{t'})$, for $t \geq t'$.

This is exactly what happens for $f(\mathbf{x}, \mathbf{v}, t) = f_t$ evolving according to the Boltzmann equation:

Boltzmann's \mathcal{H} -theorem :

$$\begin{aligned} \frac{d}{dt} \left\{ - \int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} f_t(\mathbf{x}, \mathbf{v}) \log f_t(\mathbf{x}, \mathbf{v}) \right\} \\ = \frac{d}{dt} s_{\text{gas}}(f_t) = b\mathcal{I}(f_t) \geq 0, \end{aligned} \quad (15)$$

with equality holding only when f_t is a local Maxwellian, i.e. ρ and T can be functions of x .

As put by Boltzmann⁶:

"In one respect we have even generalized the entropy principle here, in that we have been able to define the entropy in a gas that is not in a stationary state."

⁶Bo98

Note that the rate of increase of entropy in (15) is proportional to $b = \lim_{\text{BG}} Nd^2$. If one takes the limit $N \rightarrow \infty$, $d \rightarrow 0$ in such a way that $Nd^2 \rightarrow 0$ then the time derivative of S_B given in (15) is equal to zero. The reason for this is that as b gets smaller the time between collisions gets larger and when $b \rightarrow 0$ this time becomes infinite.

On the other hand we expect that for any $b > 0$,

$$\lim_{t \rightarrow \infty} f_t(\mathbf{x}, \mathbf{v}) = f_{\text{eq}}(\mathbf{x}, \mathbf{v}) \quad (16)$$

and thus also that

$$\lim_{t \rightarrow \infty} s_{\text{gas}}(f_t) = s_{\text{gas}}(f_{\text{eq}}) \quad (17)$$

so that if we first take the limit $t \rightarrow \infty$ the change in $s_{\text{gas}}(f)$ is independent of b . In fact for $f_0(\mathbf{x}, \mathbf{v})$ independent of v one can simply rescale time by b , $\tau = t/b$ and f_τ in (14) and (15) then become independent of b .

Furthermore as we shall show below, the entropy $S_B(f)$ as defined in (8) can change with time, even when $b = 0$. The entropy given in (9) in terms of a smooth one particle distribution $f(x, v, t)$ does not capture all the features of the evolution of macrostates, with $|\Delta_\alpha| > 0$ essential for the increase of the Boltzmann entropy, i.e. the increase of $|\Gamma_M(t)|$ with t . This will involve for $|\Delta_\alpha| > 0$ not only contributions from collisions, as specified by (15), but also contributions from spreading in physical space.

In fact even an **ideal gas** with $b \equiv 0$ will exhibit spreading in physical space and an increase in Boltzmann's entropy if one considers the evolution of macrostates of systems with initially nonuniform spatial density.

The relative contribution of the two mechanisms when $b \neq 0$ depends on the magnitudes of b and of $|\Delta_\alpha|$.

The case $b = 0$ has been investigated recently numerically and analytically for a one dimensional ideal gas in a box⁷. We considered a fixed decomposition of the one particle phase space (x, v) into rectangles of sizes $|\Delta_\alpha| = \Delta x \Delta v$, and defined the macrostate M , by the $\{f_\alpha\}$, $f_\alpha = \frac{N_\alpha}{|\Delta_\alpha|}$ where N_α is the number of particles in the box α . We then have, for large N , so as in (8),

$$S_B(M) = - \sum_{\alpha} |\Delta_\alpha| f_\alpha \log f_\alpha + Const \quad (18)$$

up to a constant. (f_α here differs from that defined earlier by a factor N)

⁷S. Chakraborti, A. Dhar, S. Goldstein, A. Kundu and J. Lebowitz (arXiv:2109.07742)

The time evolution of $S_B(M(X_t))$ when X_0 is chosen at random from an initial Γ_{M_0} corresponding to the phase space region where all N particles are in in the left half of the box with energy E approximately $N\epsilon_0$, $\epsilon_0 = 1.25$ corresponding to a temperature 2.5, is shown in Figure 1 where $s_B^f(t) = \frac{1}{N} S_B(M(X_t))$.

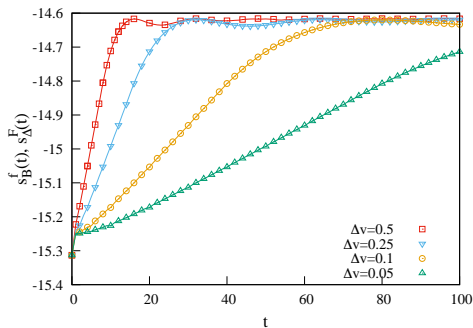


Figure 1: A comparison between $s_B^f(t)$ obtained from simulation of a single realization, and $s_Delta^F(t)$ obtained from an ensemble average, plotted as a function of time during free expansion.

For evaluating $s_B^f(t)$ we use numerical simulation of a single initial condition $X(0)$ picked at random from Γ_{M_0} for $N = 10^7$ in a box of size $L = 4$ (arbitrary units). We compute $s_B^f(t)$ for different grid sizes $|\Delta_\alpha| = \Delta x \Delta v$ by keeping $\Delta x = 0.5$ fixed and varying $\Delta v = 0.5$ (red empty circles), 0.25 (blue empty inverted triangles), 0.1 (yellow empty circles), and 0.05 (green empty triangles).

The solid lines, $s_\Delta^F(t)$, are the Gibbs-Shanon entropies obtained analytically from a coarse grained one particle density in the (x, v) space. That is we set

$$F(x, v, 0) = \sum_{i=1}^N \langle \delta(x - r_i) \delta(v - v_i) \rangle, \quad (19)$$

where the average is over the uniform microcanonical density for $X = \{r_1, \dots, r_N, v_1, \dots, v_N\}$ in Γ_{M_0} . We then evolve F according to Eq. (14) with $b = 0$ and then coarse grain over cells Δ_α . Changing Δx only affects s_B^f for early times as the density soon becomes uniform.

The evolution of an ideal gas on the interval $[0, L]$ can be mapped, see (CDGKL), into the evolution on a circle of circumference $2L$ and for simplicity of notation we shall sometimes set $2L = 1$. This does not affect anything relevant, provided we replace F below by its images under the mapping.

Figure 1 suggests that $s_B^f(t) = s_B^f(0)$ when $\Delta v \rightarrow 0$ for any fixed t . This is similar to what we found in (15) for $b = 0$ and $|\Delta| = 0$.

Note however that for each fixed Δv , no matter how small, $s_B^f(t)$ seems to go, as $t \rightarrow \infty$, to a final equilibrium value, which for the initial condition considered here is just $s_B^f(0) + \log 2$ as expected from thermodynamics.

In fact the different curves $s_B^f(t)$ collapse to a single curve when t is rescaled $t \sim \frac{\tau}{\Delta v}$, see Figure.

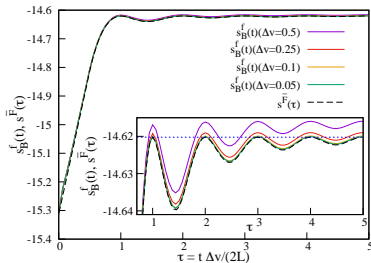


Figure 2: The figure shows a collapse of the data presented in Figure 1 for different values of Δv , on plotting the entropy as a function of the scaled time $\tau = t\Delta v/(2L)$. Inset: A zoom up of the plot. The horizontal dotted line corresponds to the final equilibrium entropy.

The dashed line is the graph of $s^{\overline{F}}(\tau)$, defined below for which it can be shown that

$$s^{\overline{F}}(\tau) = \lim_{\Delta v \rightarrow 0} s^F(2L\tau/\Delta v). \quad (20)$$

The quantity $s^{\bar{F}}(\tau)$ is given by

$$s^{\bar{F}}(\tau) = -\frac{1}{N} \int \bar{F}(x, v, \tau) \ln \bar{F}(x, v, \tau) dx dv \quad (21)$$

where setting $2L = 1$, and considering the motion in a periodic box of unit length,

$$\bar{F}(x, v, \tau) = \frac{1}{\tau} \int_0^\tau F(x - x', v, 0) dx'. \quad (22)$$

Setting

$$F(x, v, 0) = \rho h(v)[1 + \phi(x, v)], \quad (23)$$

$$\phi(x, v) = \phi(x + 1, v), \quad \int_0^1 \phi(x, v) dx = 0.$$

$$\begin{aligned} \bar{F}(x, v) &= \rho h(v) \left[1 + \frac{1}{\tau} \int_0^\tau \phi(x - x', v) dx' \right] \\ &= \rho h(v) \left[1 + \frac{1}{\tau} \psi(x, v, \tau) \right], \end{aligned} \quad (24)$$

where $\psi(x, v, \tau)$ is periodic in τ with period 1 with

$$\psi(x, v, n) = 0, \quad \text{for } n = 1, 2, 3, \dots \quad (25)$$

This yields the $s\bar{F}(\tau)$ plotted in Figure 2 for the initial condition used in Figure 1. The maxima, all of equal height occur at $\tau = 1, 2, \dots$

The spatial time evolution of an ideal gas in a torus is analyzed in detail in a very nice paper by S. De Bievre and P.E. Parris⁸. They consider an initial distribution of N point particles with a product measure $\prod f_0(r_i, v_i)$, corresponding to a uniform density in part of a unit torus (see figure 3)

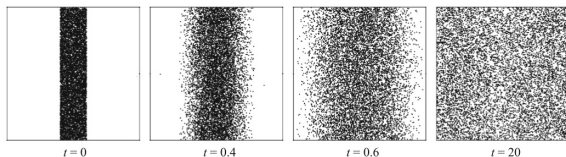


Figure 3: (From BP) Numerical simulation of the free expansion on the 2-torus of a non-interacting gas of 10^4 particles having a thermal distribution of momenta with mean thermal speed equal to unity, initially confined in the horizontal direction to the region $0.4 < x < 0.6$, at the sequence of times indicated.

and a “smooth” velocity distribution, say Maxwellian with variance 1.

⁸BiPa17

To define the macro state M_f BP divide the unit torus into \mathcal{L} squares, D_j , $j = 1, \dots, \mathcal{L}$, of area D each, and specify the fraction of particles in each region with uncertainty ϵ . M_{eq} then corresponds to “uniform density”, i.e. the fraction f_j of particles in D_j , satisfy $|f_j - D| < \epsilon$, $\epsilon > 0$, for **every** j .

Fixing \mathcal{L} and ϵ , BP prove that a system picked at random from the initial Γ_{M_f} will, with probability, $P \geq 1 - \delta_N$, $\delta_N = Le^{-\frac{1}{4}\epsilon^2 N}$, uniformly spread out, i.e. be in equilibrium, for an exponentially long time period t , $\tau_1 < t < \tau_2$. Here τ_1 is of order 1 and τ_2 is exponentially large in N , corresponding to Poincaré recurrence time.

This is what is meant by the approach to equilibrium, i.e. a uniform distribution, being **typical** behavior for phase points in the initial macrostate.

I highly recommend this paper.

More General Macroscopic Equations

Going beyond the examples described above suppose, more generally, that the time evolution of the macrostate M , given by $M(X(t)) = M_t$, effectively satisfies an autonomous deterministic time asymmetric equation, such as the diffusion or the heat equation. (I shall consider here for simplicity macrostates M which are invariant under velocity reversal.)

Having such an equation means that if $t_3 > t_2 > t_1$, then the microscopic dynamics T_t carries almost all of $\Gamma_{M_{t_1}} = \Gamma_{M_1}$, etc., inside Γ_{M_2} and Γ_{M_2} inside Γ_{M_3} , i.e. $T_{t_2-t_1}\Gamma_{M_1} \subset \Gamma_{M_2}$ and $T_{t_3-t_2}\Gamma_{M_2} \subset \Gamma_{M_3}$, with *negligible error*. Put otherwise a typical phase point in Γ_{M_1} will go to Γ_{M_2} and then to Γ_{M_3} , i.e. $T_{t_3-t_1}\Gamma_{M_1} \subset \Gamma_{M_3}$, c.f. [Go04].

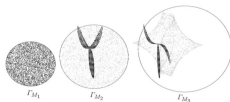


Figure 4: Time evolution of Γ_{M_1}

The fact that phase space volume is conserved by the Hamiltonian time evolution implies that $|\Gamma_{M_1}| \leq |\Gamma_{M_2}| \leq |\Gamma_{M_3}|$, and thus that $S_B(M_3) \geq S_B(M_2) \geq S_B(M_1)$.

Hence the solution of any deterministic macroscopic equation for M_t has to satisfy the inequality⁹ $\frac{d}{dt} S_B(M_t) \geq 0$, exactly what Boltzmann showed for the BE.

⁹Go04,Pe70

We note that the existence of such a macroscopic equation implies (at least insofar as the macro-variables are concerned) that the phase points in the region in Γ_2 coming from Γ_1 behave, forward in time, as microstates typical of Γ_2 .

They are, however, very atypical backwards in time. Thus if we reverse all the velocities in Γ_2 , then at a later time, $t' = t_2 + (t_2 - t_1)$ all of the points initially in Γ_{M_1} will again be in Γ_{M_1} (with their velocities reversed), a smaller region than Γ_{M_2} , while $|\Gamma_{M_{t'}}| \geq |\Gamma_{M_2}|$.

The reason for this asymmetry in typical behaviors is due in our examples to the choice of initial conditions. That is, starting out at t_1 with a nonequilibrium system in an initial micro-state $X \in \Gamma_{M_1}$ we showed, for X typical of Γ_{M_1} , that $X(t)$ will continue to be typical of M_t insofar as times greater than t_1 are concerned but obviously not for the subset of M_t corresponding to the microstates in $T_{t-t_1}\Gamma_{M_1}$ with **reversed** velocities.

If we could indeed **perfectly** reverse all the velocities in a macroscopic system out of equilibrium and keep the system **perfectly** isolated afterwards we would indeed have a situation in which entropy decreases. This illustrates the fact that the second law holds only for **typical** behavior.

But what about real life situations such as the rain dissolving a piece of paper or a meteor hitting the moon?

What corresponds to an appropriate choice of initial time and initial low entropy state? Somewhat surprisingly, if one thinks hard about it, one is pushed to consider the very beginning of the universe we live in.

This would correspond according to our current physical theories to the time just after the “Big Bang”. The importance of initial conditions, Big Bang or not, was already fully understood by Boltzmann and others as the quotes below show.

Initial Conditions

*“From the fact that the differential equations of mechanics are left unchanged by reversing the sign of time without changing anything else, Herr Ostwald concludes that the mechanical view of the world cannot explain why natural processes always run preferentially in a definite direction. **But such a view appears to me to overlook that mechanical events are determined not only by differential equations, but also by initial conditions.** In direct contrast to Herr Ostwald I have called it one of the most brilliant confirmations of the mechanical view of Nature that it provides an extraordinarily good picture of the dissipation of energy, as long as one assumes that the world began in an initial state satisfying certain conditions. I have called this state an improbable state.”*

— L. Boltzmann¹⁰

¹⁰Bo97

“It is necessary to add to the physical laws the hypothesis that, in the past the universe was more ordered in the technical sense, [i.e. low S_B] than it is today ... to make an understanding of irreversibility.”

— R.P. Feynman¹¹

¹¹Fe67

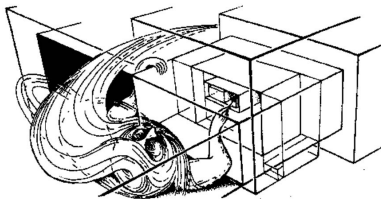


Figure 5: “Creation of the universe: a fanciful description! The Creator’s pin has to find a tiny box, just 1 part in $10^{10^{123}}$ of the entire phase-space volume, in order to create a universe with as special a Big Bang as we actually find.” from R. Penrose, *The Emperor’s New Mind*

The “tiny box” in the figure is a macrostate with low S_B . N.B. It is not necessary to select a particular microstate. Almost all microstates in a low-entropy macrostate will behave in a similar way.

It may be relevant to mention here a question I was asked during a talk I gave on the subject:

Q: What does the initial state of the universe have to do with the fact that when I put my sugar cube in my tea it dissolves irreversibly?

A: Nothing directly. But the fact that you, the sugar cube and the tea are all here is a consequence of the initial low entropy state of the universe.

Boltzmann vs. Gibbs Entropies

Given an ensemble (probability) density $\mu(X)$, $X \in \Gamma$, the Gibbs-Shannon entropy is given by

$$S_\mu \equiv - \int_\Gamma \mu \log \mu \, dX. \quad (26)$$

Clearly if $\mu = \tilde{\mu}_M$, where

$$\tilde{\mu}_M = \begin{cases} |\Gamma_M|^{-1}, & \text{if } X \in \Gamma_M; \\ 0, & \text{otherwise} \end{cases} \quad (27)$$

then

$$S_G(\tilde{\mu}_M) = \log |\Gamma_M| = S_B(M). \quad (28)$$

This is essentially the case for the microcanonical ensemble since $\Gamma_E \simeq \Gamma_{M_{\text{eq}}}$. By the equivalence of ensembles for macroscopic systems the same is true for the canonical and other Gibbs ensembles.

Thus the Gibbs and Boltzmann entropies are equal for equilibrium systems.

However, as $\mu = \mu_t$ evolves via the Hamiltonian dynamics for isolated systems $S_G(\mu)$ does not change in time. $S_G(\mu)$ is therefore “useless” for such systems not in equilibrium, while $S_B(M(X_t))$ captures the essence of typical macroscopic behavior. In particular it satisfies the second law of thermodynamics.



Figure 6: Boltzmann's grave in Zentralfriedhof, Vienna, with bust and entropy formula

Quantum Systems

Let me turn now to quantum systems. These are very different on the microscopic level from, but quite similar on the macroscopic level to, classical systems.

The first question is: what microstates should we associate with a physically isolated macroscopic system in a definite macrostate? Unfortunately there is no consensus on this, even a century after the birth of quantum mechanics, and its perfect success in explaining and predicting microscopic phenomena.

There is however no doubt that, as put by Einstein, Boltzmann's ideas are applicable to the quantum (real) world.

I will assume for this talk that by the microstate of a macroscopic system with an energy in a narrow interval $(E, E + \Delta E)$ we mean a wave function $\psi \in \mathcal{H}_E$, where \mathcal{H}_E is a shell in Hilbert space of thickness ΔE , i.e. \mathcal{H}_E consists of all linear combination of energy eigenfunctions in the range $(E, E + \Delta E)$, $\Delta E \ll E$ but very large compared to the spacing between levels.

This is not perfect (problems with Schrödinger's Cat) but it will have to do for the present (see below). Using a density matrix with eigenstates in \mathcal{H}_E would give similar results.

The next question then is which ψ correspond to the system being in macroscopic thermal equilibrium (MATE), i.e. what is the analog of a classical microstate X lying in $\Gamma_{M_{\text{eq}}}$.

Following von Neumann¹², we take the macro-observables corresponding to the macrostate M to commute with each other. We assume that this can be achieved by suitably “rounding off”, i.e. coarse-graining, the operators representing the macro-observables.

¹²Chapter 5 of Ne55

The coarse-grained energy operator commutes with the other coarse-grained macro-observables, which I shall also denote by M . Thus all M 's can be regarded as operators on \mathcal{H}_E . Their joint spectral decomposition defines an orthogonal decomposition

$$\mathcal{H}_E = \bigoplus_{\nu} \mathcal{H}_{\nu}, \quad (29)$$

Each subspace \mathcal{H}_{ν} consists of all linear combinations of the joint eigenvectors of the macro-observables whose eigenvalues lie in a narrow range. These subspaces \mathcal{H}_{ν} correspond to the different macrostates and the orthogonal decomposition (29) of \mathcal{H}_E corresponds to the division of the classical energy shell Γ_E into disjoint regions Γ_M .

A system is in a macrostate M_ν if its wave function ψ is “close” to \mathcal{H}_ν , i.e.

$$\langle \psi | P_\nu | \psi \rangle \geq 1 - \delta, \quad \delta \ll 1, \quad (30)$$

with P_ν being the projection to \mathcal{H}_ν .

There will of course be ψ 's in \mathcal{H}_E which are a superposition of ψ 's in different macrostates: Schrödinger's Cat problem mentioned earlier.

To remedy this one has to go beyond the Copenhagen doctrine that the wave function is a complete description¹³. For the present let me say that I would interpret such ψ 's when they arise physically as giving probabilities $\langle \psi | P_\nu | \psi \rangle$ of being in different macrostates, M_ν .

¹³Be87,Go98

The analog of the phase space volume $|\Gamma_M|$ is the dimension d_ν of each macro space \mathcal{H}_ν .

As in the classical case, it is generally true that one of the \mathcal{H}_ν , denoted \mathcal{H}_{eq} , has most of the dimensions of \mathcal{H}_E , i.e.,

$$\frac{\dim \mathcal{H}_{\text{eq}}}{\dim \mathcal{H}_E} = 1 - \varepsilon \quad (31)$$

with $\varepsilon \ll 1$.

The Boltzmann entropy S_B of a system in a macrostate M_ν is given by the log of the dimension of the macro space \mathcal{H}_ν ;

$$S_B(M_\nu) = \log d_\nu. \quad (32)$$

Given this correspondence between partitioning Γ_E and decomposing \mathcal{H}_E most everything we said about isolated classical macroscopic systems then also holds for quantum systems. In particular for $\varepsilon \ll \delta$, most $\psi \in \mathcal{H}_E$ are in MATE.

The Boltzmann argument for increase in entropy of isolated macroscopic systems out of equilibrium is then similar to that in the classical case¹⁴.

When I say “most ψ ”, I mean with respect to a uniform measure on the unit sphere in \mathcal{H}_E . This measure on “wave functions” was considered already by Schrödinger and particularly by Felix Bloch¹⁵. It yields the microcanonical density matrix ρ^{mc} but goes beyond it, in ascribing probabilities to any subset of \mathcal{H}_E .

¹⁴Gr94

¹⁵Go06

There is however also something beyond MATE which can be used for the characterization of quantum systems in equilibrium.

Unlike classical systems, where any subsystem of a system in a microstate X is also in a microstate X_S , having definite positions and velocities, a subsystem S of a quantum system with a wave function ψ will usually not be described by a wave function, but rather by a density matrix ρ_S^ψ , where

$$\rho_S^\psi = \text{tr}_{S^c} |\psi\rangle\langle\psi| \quad (33)$$

is the reduced density matrix of S obtained by tracing out the complement S^c of S .

We can now define¹⁶ a system with wave function ψ to be in microscopic thermal equilibrium (MITE) if, for any not-too-large subsystem S , say subsystems with linear dimension $l < l_0$, for an appropriate l_0 , the reduced density matrix of S is close to the thermal equilibrium density matrix of S

$$\rho_S^\psi \approx \rho_S^{\text{mc}}, \quad (34)$$

$$\rho_S^{\text{mc}} = \text{tr}_{S^c} \rho^{\text{mc}}, \quad (35)$$

where ρ^{mc} is the microcanonical density matrix corresponding to a uniform distribution over energy eigenstates in \mathcal{H}_E . For macroscopic systems ρ_S^{mc} can be replaced by ρ_S^{ca} , where ρ^{ca} is the canonical density matrix.

The distinction between MITE and MATE is important for systems with many-body localization (MBL) for which most, if not all, the energy eigenfunctions fail to be in MITE while necessarily most of them, but not all, are in MATE.

¹⁶Go17

The argument for most energy eigenfunctions being in MATE is based on the fact that, calling D the dimension of \mathcal{H}_E , we have for energy eigenfunctions $|n\rangle$

$$\frac{1}{D} \sum_{n=1}^D \langle n | P_{\nu_{\text{eq}}} | n \rangle = \frac{1}{D} \text{tr}(P_{\nu_{\text{eq}}}) = 1 - \varepsilon \quad (36)$$

Noting that $\langle n | P_{\nu_{\text{eq}}} | n \rangle \leq 1$, the average being close to 1 means that most eigenstates are close to $\mathcal{H}_{\nu_{\text{eq}}}$. This is consistent with the Eigenstate Thermalization Hypothesis (ETH).

In fact for generic macroscopic systems, including those with MBL, most wave functions in an energy shell are in both MATE and MITE. This follows from the following result.

Canonical Typicality

Consider an isolated system consisting of two parts. Call them system 1 and 2 or system and reservoir. Then¹⁷ we have the following result.

Let H be the Hamiltonian of the whole system and let the number of particles in system 1 and 2 be $N_1 \ll N_2$. Let $\mathcal{H}_E \subset \mathcal{H}_1 \otimes \mathcal{H}_2$ be an energy shell. Then for most $\psi \in \mathcal{H}_E$ with $\|\psi\| = 1$,

$$\mathrm{tr}_2 |\psi\rangle\langle\psi| \approx \mathrm{tr}_2 \rho^{\mathrm{mc}}, \quad (37)$$

where ρ^{mc} is the microcanonical density matrix of the whole system at energy E , i.e. equal weight to all energy eigenstates in \mathcal{H}_E .

When the interaction between systems 1 and 2 is weak then, as is well known, $\mathrm{tr}_2 \rho^{\mathrm{mc}} \approx \frac{1}{Z} e^{-\beta H_1}$ for $\beta = \beta(E) = dS_{\mathrm{eq}}(E)/dE$.

¹⁷Go06,Le08

The theorem says that most wave functions in the energy shell \mathcal{H}_E are both in MATE and in MITE. In fact for macroscopic systems one can show that MITE implies MATE.

The opposite is however not true.

This is particularly relevant when one considers energy eigenfunctions $|n\rangle$. While most energy eigenstates, including those for systems with MBL must, as shown, generally be in MATE, most energy eigenfunctions for systems with MBL are not in MITE.

Interestingly MITE has been found experimentally and computationally to hold for systems with Hilbert spaces with dimension as small as 100 or so, for which the motion of macrostates is not really appropriate.

This brings up the question of how to apply what I have discussed here to systems with a small number of degrees of freedom. When considering such systems it is relevant to remember that probabilities of $\mathcal{O}(10^{-6})$ might not be so different in practice from probabilities of $\mathcal{O}(10^{-20})$.

I will not discuss this or the related issues of “stochastic thermodynamics” here.

If MATE-ETH holds strictly, i.e., if *all* energy eigenstates in \mathcal{H}_E are in MATE, then every state $\psi \in \mathcal{H}_E$ will sooner or later reach MATE and spend most of the time in MATE in the long run. That is because, writing $\overline{f(t)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(t) dt$ for time averages, $|n\rangle$ for the energy eigenstate with eigenvalue E_n and $\psi_t = e^{-iHt}\psi$,

$$\overline{\langle \psi_t | P_{\text{eq}} | \psi_t \rangle} = \sum_{n, n'} \langle \psi | n \rangle \overline{e^{iE_n t} \langle n | P_{\text{eq}} | n' \rangle e^{-iE_{n'} t} \langle n' | \psi \rangle} \quad (38)$$

$$= \sum_n |\langle \psi | n \rangle|^2 \langle n | P_{\text{eq}} | n \rangle \geq \sum_n |\langle \psi | n \rangle|^2 (1 - \delta) \quad (39)$$

$$= 1 - \delta, \quad (40)$$

provided H is non-degenerate, i.e., $E_n \neq E_{n'}$ for $n \neq n'$ (using $\overline{e^{iEt}} = 1$ if $E = 0$ and $= 0$ otherwise).

A similar statement is true when there is degeneracy.

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