

Boltzmann's Entropy for Macroscopic Systems: Classical and Quantum

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To the memory of Detlef Dürr

Abstract¹

Boltzmann's entropy is defined for individual macroscopic systems in a specified macrostate; equilibrium or not. In the latter case it satisfies the second law of thermodynamics which characterizes the time evolution of a typical isolated macroscopic system in a non-equilibrium macrostate. The time asymmetry of this observed evolution can be **understood** as arising from: 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.

¹Some of this work was done jointly with S. Goldstein, D. Huse, and R. Tumulka. 1 / 48

Introduction

An excellent summary of Boltzmann's ideas can be found in Einstein's description of Planck's reasoning leading to his discovery of the quantization of energy:

*"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 [macro] 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. Planck recognized this and applied the Boltzmann principle to a system which consists of very many resonators of the same frequency.**"²*

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” of the microstates corresponding to that macrostate.

Since Boltzmann was working in the framework of classical mechanics, the fundamental theory when Boltzmann first did this³, Boltzmann let the “number” of microstates go to infinity and replaced the number by something proportional to phase space volume. Of course when Einstein was describing Boltzmann’s work, the fundamental theory was quantum mechanics in which “number” was right.

³Bo 1877

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. Note the quotation marks around the word “probability” in the Einstein quote.

Once one accepts the applicability of these measures (ensembles) to physical systems they can be used to predict the typical behavior of individual macroscopic systems *and* not just some average behavior.

The observed behavior does not require explanations based on ergodicity, time averaging, or subjective information theory.

Classical Systems

In classical mechanics, the microstate of a 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 $H(X) = E$.

This time evolution, $T_t X = X(t)$, is reversible: given $X = (\mathbf{r}_1, \mathbf{v}_1, \dots, \mathbf{r}_N, \mathbf{v}_N)$ define $RX = (\mathbf{r}_1, -\mathbf{v}_1, \dots, \mathbf{r}_N, -\mathbf{v}_N)$ then

$$T_s R T_s X = RX. \quad (2)$$

A macroscopic system is one with “very large” N , say $N \gtrsim 10^{20}$. For such systems it is more appropriate to replace the energy surface by a thin shell surrounding that surface, to which I will always refer as Γ_E . The micro-canonical ensemble is a uniform measure on Γ_E .

For macroscopic systems an overwhelming majority of the microstates in the micro-canonical ensemble give the same “thermodynamic” behavior: such behavior is typical, i.e. it has probability close to one for this probability distribution.

In fact, the fraction of systems with noticeable macroscopic deviations from the average behavior, computed in such an ensemble, is exponentially small in the number of degrees of freedom of the system.

The functions on the phase space which correspond to such “thermodynamic” behavior are sums of terms which depend only on the coordinates and momenta of a few particles, e.g. the kinetic energy.

Macrostates

To describe the macroscopic state of such a system of N particles in a box V , we make use of a much cruder description than that provided by the microstate X . We shall denote by M such a macroscopic description.

In general we can describe a macrostate M by specifying a set of macrovariables $M(X) = \{M_1(X), M_2(X), \dots, M_n(X)\}$, with resolution $\Delta M = \{\Delta M_j\}$. We identify these macrostates with the elements of a partition of the phase space into sets Γ of the form

$$\Gamma_M = \{X | M_j \leq M_j(X) \leq M_j + \Delta M_j, j = 1, \dots, n\}. \quad (3)$$

These provide a coarse-grained description in the sense that many different X correspond to the same Γ_M . This is the number Z that Einstein talks about.

It can be shown⁴ that for all reasonable choices 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} ,

$$\frac{|\Gamma_{M_{\text{eq}}}|}{|\Gamma_E|} = 1 - \varepsilon \quad (4)$$

with $\varepsilon \ll 1$.

A system in a microstate X is then in macroscopic thermal equilibrium relative to the choice of the M 's iff $X \in \Gamma_{M_{\text{eq}}}$. The volume of all the Γ_M specifying nonequilibrium states is very much smaller than $|\Gamma_E|$. This is essentially a consequence of the law of large numbers.

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

⁴La73

Nonequilibrium States

Thus, most microstates in Γ_E of a macroscopic system correspond to the system being in equilibrium.

Fortunately there are also microstates which correspond to macroscopic systems which are out of equilibrium (or we would not be here).

Consider now the time evolution of the macro variables $M(X(t))$ when the system is in the microstate $X(t_0) \in \Gamma_M$, $M \neq M_{\text{eq}}$, at an “initial” time t_0 , and is isolated for $t > t_0$.

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 a microstate $X(t_0)$, typical wrt a uniform measure on Γ_M , will be such that $|\Gamma_{M(X(t))}|$ will not decrease (on a macroscopic scale) for $t > t_0$.

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 defined the (Boltzmann) entropy of a macroscopic system in a microstate X as

$$S_B(X) = \log |\Gamma_{M(X)}| = S_B(M(X)). \quad (5)$$

The entropy of the equilibrium macrostate

$$S_B(M_{\text{eq}}) = \log |\Gamma_{M_{\text{eq}}}| \simeq \log |\Gamma_E| \quad (6)$$

Boltzmann then showed that $S_B(M_{\text{eq}})$ agrees with the Clausius thermodynamic entropy of a gas in equilibrium, which could be measured (up to some constant) for gases at room temperature where quantum effects can be neglected.

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 scales⁵.

A proof would be provided by the rigorous derivation from the microscopic dynamics of the kinetic and hydrodynamic equations⁶ 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.

⁵As Mark Kac said: an argument convinces a reasonable person, a proof convinces a stubborn one.

⁶such as the heat equation, Navier-Stokes equations, etc.

I will not go into Lanford's derivation here. This is very clearly described in Lanford's article of 1976 which is highly recommended⁷. I will instead go on to describe some recent work on the time evolution of the Boltzmann entropy for a one dimensional ideal gas of N particles in a box⁸.

We considered a decomposition of the one particle phase space (x, v) into rectangles α of sizes $|\Delta_\alpha| = \Delta x \Delta v$, and defined the macrostate M_f , 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 ,

$$\log |\Gamma_{M_f}| = S_B(M_f) = - \sum_{\alpha} |\Delta_\alpha| f_\alpha \log f_\alpha \quad (7)$$

up to a constant. This was computed by Boltzmann⁹.

⁷La76

⁸S. Chakraborti, A. Dhar, S. Goldstein, A. Kundu and J. Lebowitz (arXiv:2109.07742)

⁹Bo 1897

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 $s_B^f(t) = \frac{1}{N} S_B(M(X_t))$.

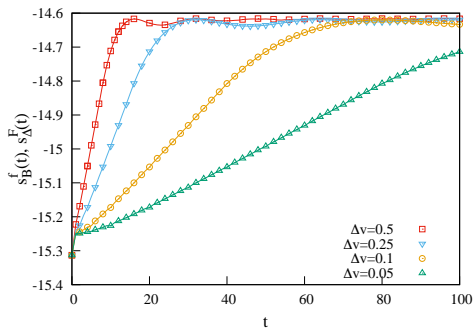


Figure 1: A comparison between $s_B^f(t)$ obtained from simulation of a single realization, and $s_Delta^F(t)$ obtained from an ensemble average, plotted as a function of time during free expansion.

For evaluating $s_B^f(t)$ we used 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 coarsegrained one particle density in the (x, v) space. That is we set

$$F(x, v, 0) = \sum_{i=1}^N \langle \delta(x - r_i) \delta(v - v_i) \rangle, \quad (8)$$

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 the equation

$$\frac{\partial F(x, v, t)}{\partial t} + v \frac{\partial F}{\partial x} = 0 \quad (9)$$

and then coarsegrain over cells Δ_α .

Figure 1 might suggest that $s_B^f(t) = s_B^f(0)$ when $\Delta v \rightarrow 0$ for any fixed t .

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 for a classical ideal gas.

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 2.

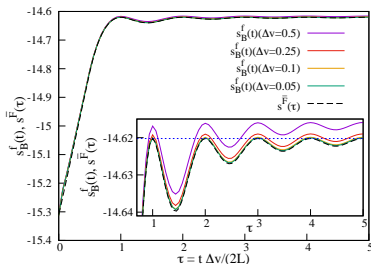


Figure 2: The figure shows a collapse of the data presented in Figure 1 for different values of Δv , on plotting the entropy as a function of the scaled time $\tau = t\Delta v/(2L)$. Inset: A zoom up of the plot. The horizontal dotted line corresponds to the final equilibrium entropy.

The dashed line shows the analytically computed $\lim_{\Delta v \rightarrow 0} s_{\Delta}^F(t)$ which agrees with the simulation results.

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. Parrisi¹⁰. 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)

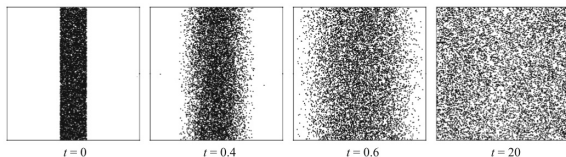


Figure 3: (From BP) Numerical simulation of the free expansion on the 2-torus of a non-interacting gas of 10^4 particles having a thermal distribution of momenta with mean thermal speed equal to unity, initially confined in the horizontal direction to the region $0.4 < x < 0.6$, at the sequence of times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

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

¹⁰BiPa17

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.

General Macroscopic Equations

Going beyond the idealized example described above suppose 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 an equation like that means that if $t_3 > t_2 > t_1$, then the microscopic dynamics T_t carries $\Gamma_{M_{t_1}} = \Gamma_{M_1}$, 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. $T_{t_3-t_1}\Gamma_{M_1} \subset \Gamma_{M_3}$.

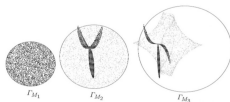


Figure 4: Time evolution of Γ_{M_1}

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 inequality¹¹ $\frac{d}{dt} S_B(M_t) \geq 0$, exactly what Boltzmann showed for the BE.

¹¹Go04,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 behavior of macroscopic systems is due to the choice of initial conditions. That is, starting out at t_1 with a nonequilibrium system in an initial micro-state $X \in \Gamma_{M_1}$ typical of Γ_{M_1} , $X(t)$ 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.

In fact if we could **perfectly** reverse all the velocities in a macroscopic system out of equilibrium and keep the system **perfectly** isolated afterwards we would 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?

What corresponds to an appropriate choice of initial time and initial conditions for which one can, in fact has to, assume that at that time the state X is atypical of Γ_E but typical of Γ_M for some nonequilibrium M ? 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. Boltzmann¹²

¹²Bo97

“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. Feynman¹³

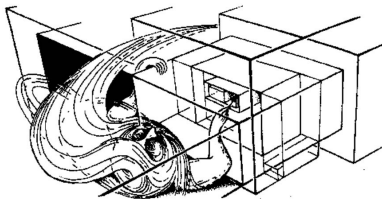


Figure 5: “Creation of the universe: a fanciful description! The Creator’s pin has to find a tiny box, just 1 part in $10^{10^{123}}$ of the entire phase-space volume, in order to create a universe with as special a Big Bang as we actually find.” from R. Penrose, *The Emperor’s New Mind*

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

$$S_\mu \equiv - \int_\Gamma \mu \log \mu \, dX. \quad (10)$$

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

$$\tilde{\mu}_M = \begin{cases} |\Gamma_M|^{-1}, & \text{if } X \in \Gamma_M; \\ 0, & \text{otherwise} \end{cases} \quad (11)$$

then

$$S_G(\tilde{\mu}_M) = \log |\Gamma_M| = S_B(M). \quad (12)$$

This is essentially the case for the microcanonical ensemble since $\Gamma_E \simeq \Gamma_{M_{\text{eq}}}$.

For macroscopic systems the canonical and other equilibrium ensembles, have the same Gibbs entropy as the microcanonical one to leading order in N . This follows from the fact that these measures are concentrated on a narrow energy shell: equivalence of ensembles.

However, as $\mu = \mu_t$ evolves via the Hamiltonian dynamics for isolated systems $S_G(\mu_t)$ does not change in time. $S_G(\mu_t)$ 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.

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 is the best quantum description of the microstate of a physically isolated macroscopic system?

I will assume for this talk that the microstate of a macroscopic system with an energy in a narrow interval $(E, E + \Delta E)$ to be 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 a macrostate M , i.e. what is the analog of a classical microstate X lying in Γ_M .

Following von Neumann¹⁴, 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. (This may not always be possible as when we consider the quantum analog of the macrostate M_f . It is something we are working on.)

¹⁴Chapter 5 of Ne55

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

$$\mathcal{H}_E = \bigoplus_M \mathcal{H}_M, \quad (13)$$

Each subspace \mathcal{H}_M consists of all linear combinations of the joint eigenvectors of the macro-observables whose eigenvalues lie in a narrow range. These subspaces \mathcal{H}_M correspond to the different macrostates and the orthogonal decomposition (13) of \mathcal{H}_E corresponds to the division of the classical energy shell Γ_E into disjoint regions Γ_M .

We then say that a system is in a macrostate M if its wave function ψ is “close” to \mathcal{H}_M , i.e.

$$\langle \psi | P_M | \psi \rangle \geq 1 - \delta, \quad \delta \ll 1, \quad (14)$$

with P_M being the projection to \mathcal{H}_M .

As noted earlier, due to the Schrödinger’s Cat problem, there will be ψ ’s which are a superposition of ψ ’s in different macrostates.

To remedy this one has to go beyond the Copenhagen doctrine that the wave function¹⁵ is a complete description. For the present let me say that I would interpret such ψ ’s when they arise physically as giving probabilities $\langle \psi | P_M | \psi \rangle$ of being in different macrostates, M . This is part way to Bohmian mechanics: for macroscopic systems we need to specify M in addition to ψ when the latter is ambiguous. Of course Detlef went all the way.

¹⁵Be87,Go98,Du09

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

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

$$S_B(M) = \log d_M. \quad (15)$$

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

$$\frac{\dim \mathcal{H}_{\text{eq}}}{\dim \mathcal{H}_E} = 1 - \varepsilon \quad (16)$$

with $\varepsilon \ll 1$.

Hence

$$S_B(M_{\text{eq}}) = \log(\dim \mathcal{H}_{\text{eq}}) \simeq \log(\dim \mathcal{H}_E). \quad (17)$$

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 macroscopic thermal equilibrium (MATE).

The Boltzmann argument for increase in entropy of isolated macroscopic systems out of equilibrium is then similar to that in the classical case¹⁶.

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 Bloch¹⁷. It yields the microcanonical density matrix ρ^{mc} but goes beyond it, in ascribing probabilities to any subset of \mathcal{H}_E .

¹⁶Gr94

¹⁷Go06

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

$$\rho_S^\psi = \text{tr}_{S^c} |\psi\rangle\langle\psi| \quad (18)$$

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

We can now define¹⁸ 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

$$\rho_S^\psi \approx \rho_S^{\text{mc}}, \quad (19)$$

$$\rho_S^{\text{mc}} = \text{tr}_{S^c} \rho^{\text{mc}}, \quad (20)$$

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.

¹⁸Go17

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 $|n\rangle$

$$\frac{1}{D} \sum_{n=1}^D \langle n | P_{M_{\text{eq}}} | n \rangle = \frac{1}{D} \text{tr}(P_{M_{\text{eq}}}) = 1 - \varepsilon \quad (21)$$

Noting that $\langle n | P_{M_{\text{eq}}} | n \rangle \leq 1$, the average being close to 1 means that most eigenstates are close to $\mathcal{H}_{M_{\text{eq}}}$. 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. Then¹⁹ 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 $\|\psi\| = 1$,

$$\mathrm{tr}_2 |\psi\rangle\langle\psi| \approx \mathrm{tr}_2 \rho^{\mathrm{mc}}, \quad (22)$$

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 $\beta = \beta(E) = dS_{\mathrm{eq}}(E)/dE$.

¹⁹Go06,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.

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