Statistical Mechanical Ensembles and Typical Behavior of Macroscopic Systems

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Abstract

In this talk I will focus on describing, in a qualitative way, the reason why statistical mechanics is able to predict, with great certainty, behavior of macroscopic systems, both in equilibrium and out of it. I will relate this to the fact that this behavior is *typical* for systems represented by the usual Gibbs ensembles or those derived from them. These take small phase space volume to indicate small probability. I will not try to justify this here.

I thank S. Goldstein, E. Speer, and O. Penrose for very many, very helpful comments and A. Krueger for technical help with these slides. I also thank the NSF and the AFOSR for long term support.

The word typical is used in ordinary language to denote a state or behavior usually observed in a given situation. Example: glasses at room temperature are typically hard. To make this more precise we need to specify a probability distribution P over some space Ω of elements X. We can then say that an event or behavior is typical if it has probability close to 1 wrt P.

For macroscopic systems an overwhelming majority of the microstates in the micro-canonical ensemble give the same “thermodynamic” behavior: such behavior is typical.

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 will be described later.

Analogous statements hold for the (exponentially small) subsets of the micro-canonical ensemble which describe systems in nonequilibrium macrostates (to be defined below), wrt to the microcanonical measure restricted to such subsets.

In particular, this applies to subsets for which the typical behavior is the time asymmetric approach to equilibrium, encoded in the second law and observed in individual macroscopic systems.

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.

I will begin with classical systems where statistical mechanics was first developed by Boltzmann, Maxwell and their contemporaries. In fact the macroscopic behavior I will consider here is pretty much the same for classical as for quantum systems.

Classical Systems

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

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

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 $H(X) = E$.

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 linear and angular momentum are not conserved quantities.

Time Evolution

The kind of Hamiltonian I have in mind is the usual effective one describing the interaction of neutral atoms, in a cubical box $V \subset \mathbb{R}^d$, with reflecting boundaries

$$H(X) = \frac{1}{2}\sum_{i=1}^{N} \mathbf{v}_i^2 + \sum_{i<j} \phi(r_{ij}) \tag{2}$$

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\phi(r)$ a potential of the Lennard-Jones or hard sphere type. The time evolution of the microstate is given by the solution of the equations

$$\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = \mathbf{v}_i, \quad \frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t} = -\sum_{j\neq i} \frac{\partial \phi(r_{ij})}{\partial \mathbf{r}_i}, \tag{3}$$

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

$$T_s R T_s X = RX. \tag{4}$$

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, and by $M(X)$ the macrostate of the system in the microstate X. The amount of information in $M(X)$ is much smaller than that contained in the microstate X.

The exact definition of macrostates is somewhat dependent on how precise a macroscopic description we are interested in. In all cases the state M of macroscopic systems will depend only on values of certain thermodynamic functions. These are sums of terms which depend only on the coordinates and momenta of a few particles, e.g.

$$f(X) = \sum_{i=1}^{N} f_1(r_i, v_i) + \sum_{i,j=1}^{N} f_2(r_i, v_i, r_j, v_j). \tag{5}$$

As an example we may divide V into K cells, where K is large but still $K \ll N$, and define M by specifying values of some of the thermodynamic functions representing the number of particles, the momentum and the amount of energy in each cell, with some tolerance. This is a natural choice from a thermodynamic point of view but we can and shall also use more crude and more refined descriptions of macrostate.

Clearly there are many X's (in fact a continuum) which correspond to the same M. Let Γ_M be the region in Γ_E consisting of all microstates X corresponding to a given macrostate M and denote by $|\Gamma_M|$ its phase-space volume.

Taking $H(X)$ of the form (2) it can be shown[1] 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},

$$\frac{|\Gamma_{M_{\mathrm{eq}}}|}{|\Gamma_E|} = 1 - \varepsilon \tag{6}$$

with $\varepsilon \ll 1$.

A system is then in macroscopic thermal equilibrium relative to the choice of the M's iff $X \in \Gamma_{M_{\mathrm{eq}}}$. When M specifies a nonequilibrium state, $|\Gamma_M|$ is very much smaller, see Figure 1 for a generic choice of reasonable M's. This is essentially a consequence of the law of large numbers.

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[1] La73

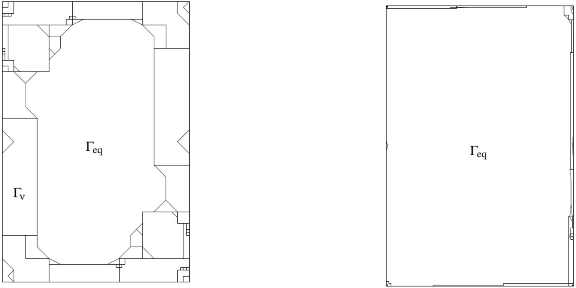

Figure 1: Schematic Picture of the decomposition of Γ_E. Here $\Gamma_{\text{eq}} \equiv \Gamma_{M_{\text{eq}}}$.

The second picture is slightly more faithful.

Neither shows the topology or differences in relative sizes of the different Γ_M's. In general, the closer M is to M_{eq} the larger Γ_M.

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

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

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.

N.B Ergodicity in the "mathematical sense" means that "all" functions, not just thermodynamic type functions have time averages equal to ensemble averages for almost all initial values. We are however only interested in the thermodynamic type functions and these can and do have the same value on different "ergodic components" of Γ_E.

Nonequilibrium States

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

As we shall see when we discuss quantum systems below, a similar statement is true for most wave functions, in fact also for most energy eigenstates, in $\mathscr{H}_E$, the energy shell of the Hilbert space.

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 macrostate $M(X(t))$ when the system is in the microstate $X(t_0) \in \Gamma_M$, $M \neq M_{\mathrm{eq}}$, 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, $M \neq M_{\mathrm{eq}}$, 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.

In fact one can argue that for any Γ_M the relative volume of the set of microstates $X \in \Gamma_M$ for which the above is false over some macroscopic time period, τ, goes to zero exponentially in the number of atoms in the system. τ should be long enough for the macrostate to undergo a macroscopically noticeable change but not longer than the age of the universe.

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

$$S_{\mathrm{B}}(X) = \log|\Gamma_{M(X)}| = S_{\mathrm{B}}(M(X)). \tag{7}$$

The entropy of the equilibrium macrostate

$$S_{\mathrm{B}}(M_{\mathrm{eq}}) = \log|\Gamma_{M_{\mathrm{eq}}}| \simeq \log|\Gamma_E| \tag{8}$$

is then the maximum value of $S_{\mathrm{B}}(M)$ over all macrostates M with energy E.

Boltzmann then showed that $S_B(M_{\mathrm{eq}})$ 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 scales[2].

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

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[2] As Mark Kac said: an argument convinces a reasonable person, a proof convinces a stubborn one

The Boltzmann Equation for Dilute Gases

Following Boltzmann, we refine the description of a macrostate M by noting that the microstate $X = \{\mathbf{r}_i, \mathbf{v}_i\}$, $i = 1, \ldots, N$, 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, centered on $(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$, of volume $|\Delta_\alpha|$, we can describe the macro (meso) states of the system $X \in \Gamma_E$ by specifying, with some leeway, the fraction of particles in each Δ_α.

Conversely given a smooth distribution $f(\mathbf{x}, \mathbf{v})$ in the one-particle space we define the macrostate M_f and the region $\Gamma_{M_f} \subset \Gamma_E$ as consisting of phase points X such that the fraction of particles in each Δ_α is given by

$$N_\alpha(X)/N \cong \int_{\Delta_\alpha} \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{v}\ f(\mathbf{x}, \mathbf{v}). \tag{9}$$

Since we are dealing with a dilute gas we can neglect the interaction energy so f determines the energy E of the macrostate M_f.

Boltzmann then used his deep physical intuition (and hints from Maxwell) to derive his eponymous equation for the time evolution of the macrostate M_f.

The reasoning behind Boltzmann's analysis and the exact derivation of the Boltzmann equation (BE) is carefully explained in Lanford's beautiful non-technical article[3]. This is one of the best mathematical-physics articles I have ever read. I strongly recommend it.

I will now give a bird's eye view of what I think is the essence of that article.

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[3] La76

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.

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

Let $f_0(\mathbf{x},\mathbf{v}) \geq 0, \mathbf{x} \in V \subset \mathbb{R}^3, \mathbf{v} \in \mathbb{R}^3$, be a smooth distribution of integral one in the one particle space.

Consider now for each N all the phase points X_N of this gas such that $X_N \in \Gamma_{M_{f_0}} \subset \Gamma_E$. Here Γ_E (and $\Gamma_{M_{f_0}}$) will have $6N$ dimensions but $f_0(\mathbf{x},\mathbf{v})$ is a fixed function on $\mathbb{R}^6$. As N increases the fraction of particles in Δ_α, is required to satisfy ever more closely $N_\alpha(X_N)/N \cong \int_{\Delta_\alpha} f_0(\mathbf{x},\mathbf{v})\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{v}$, with equality in the BG limit,

$$\lim_{\mathrm{BG}} N_\alpha(X_N)/N = \int_{\Delta_\alpha} f_0(\mathbf{x},\mathbf{v})\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{v} \tag{10}$$

Lanford's theorem then says:
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 all reasonable sets of Δ_α's

$$\lim_{BG} \frac{N_\alpha(X_N(t))}{N} = \int_{\Delta_\alpha} f(\mathbf{x}, \mathbf{v}, t) \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{v} \tag{11}$$

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

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{x}} = Q(f, f) \tag{12}$$

with initial condition $f_0(\mathbf{x}, \mathbf{v})$.

Here again typical is with respect to the uniform measure on $\Gamma_{M_{f_0}}$.

The BE gives a deterministic evolution from 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.

The Boltzmann entropy of a dilute gas in a macrostate M_f (as defined in (7)) is,

$$S_{\mathrm{B}}(f) = S_{\mathrm{B}}(M_f) = \log|\Gamma_{M_f}| \tag{13}$$

where $|\Gamma_{M_f}|$ is for an N particle system the $6N$ dimensional phase space volume of Γ_{M_f}

$S_{\mathrm{B}}(f)$ was actually computed by Boltzmann. He showed that, up to constants, this is given for a dilute gas of N particles by

$$\frac{1}{N} S_{\mathrm{B}}(f) = -\int_V \mathrm{d}\mathbf{x} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{v}\ f(\mathbf{x},\mathbf{v}) \log f(\mathbf{x},\mathbf{v}). \tag{14}$$

While (14) looks like, and is sometimes mistakenly confused with, the Gibbs-Shannon entropy per particle for a system in a product measure of the form $\prod_i f(\mathbf{x}_i, \mathbf{v}_i)$, it is conceptually not the same at all. $S_{\mathrm{B}}(f)$ is the entropy of an individual system with empirical distribution $f(\mathbf{x},\mathbf{v})$ (see below).

The maximum of $S_{\mathrm{B}}(f)$ over all f for a system of N particles in a unit volume with a given energy, which is for a dilute gas just the kinetic energy, is given by the Maxwell distribution

$$f_{\mathrm{eq}} = (2\pi kT/m)^{-3/2} \exp[-m\mathbf{v}^2/2kT] \tag{15}$$

where $kT = 2/3(E/N)$.

The distribution $f_{\mathrm{eq}}(\mathbf{x}, \mathbf{v})$ is the unique stationary solution of the BE.

In this case $\Gamma_{M_{f_{\mathrm{eq}}}} = \Gamma_{M_{\mathrm{eq}}}$ and the entropy/particle is given by

$$\frac{1}{N} S_{\mathrm{B}}(f_{\mathrm{eq}}) = \frac{3}{2} \log T - \log \frac{N}{|V|} + \mathrm{Const.} \tag{16}$$

the same as the equilibrium Clausius entropy for a dilute gas, with density $\frac{N}{|V|}$.

The second law now says that for a *typical* microstate of a dilute gas with $X(0) \in \Gamma_{M_{f_0}}$, $f_0 \neq f_{\mathrm{eq}}$, $f(\mathbf{x}, \mathbf{v}, t) = f_t$ has to be such that $S_{\mathrm{B}}(f_t) \geq S_{\mathrm{B}}(f_{t'})$, for $t \geq t'$.

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

$$\frac{\mathrm{d}}{\mathrm{d}\,t} S_{\mathrm{B}}(f_t) \geq 0, \quad \text{Boltzmann's } \mathcal{H}\text{-theorem} \tag{17}$$

As put by Boltzmann[4]:

> *"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."*

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[4] Bo98

Lanford could prove his theorem only for a time $0 < t < \tau$. This is still the case at present. In fact one can only prove the existence of smooth solutions of the BE by using Lanford's theorem and then of course only for times $t < \tau$.

The time τ for which Lanford's theorem holds is about one fifth of the mean free time between collisions, but that is a purely technical problem. This time is long enough for the Boltzmann entropy per particle to increase by a finite amount.

More General Macroscopic Equations

Going beyond the BE 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 an equation like the Boltzmann equation just discussed means that if $t_3 > t_2 > t_1$, then the microscopic dynamics T_t carries $\Gamma_{M_{t_1}} = \Gamma_{M_1}$, 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. $T_{t_3-t_1}\Gamma_{M_1} \subset \Gamma_{M_3}$.

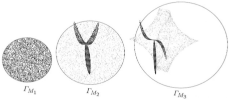

Figure 2: Time evolution of Γ_{M_1}

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 $S_{\mathrm{B}}(M_3) \geq S_{\mathrm{B}}(M_2) \geq S_{\mathrm{B}}(M_1)$.

Hence the solution of any deterministic macroscopic equation for M_t has to satisfy the inequality[5] $\frac{\mathrm{d}}{\mathrm{d}t} S_{\mathrm{B}}(M_t) \geq 0$, exactly what Boltzmann showed for the BE.

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[5] Go04,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 to initial conditions. That is, when nature or the experimentalist who is part of nature, starts out at t_1 with a nonequilibrium system in an initial state $X \in \Gamma_{M_1}$ we can assume, 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 with regard to times earlier than t_1.

This was shown explicitly in the Lanford derivation of the BE: reversing the velocities at some $t > 0$ $(t < \tau)$ violates the assumptions on the initial conditions required for the derivation of the Boltzmann equation.

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 have a violation of the second law.

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 (because it is a low entropy nonequilibrium 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. Boltzmann[6]

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[6] Bo97

> *"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. Feynman[7]

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[7] Fe67

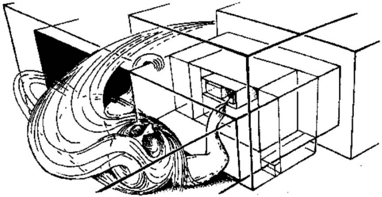

Figure 3: “Creation of the universe: a fanciful description! The Creator’s pin has to find a tiny box, just 1 part in $10^{10^{123}}$ of the entire phase-space volume, in order to create a universe with as special a Big Bang as we actually find.” from R. Penrose, *The Emperor’s New Mind*

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

$$S_\mu \equiv -\int_\Gamma \mu \log \mu \, \mathrm{d}X. \tag{18}$$

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

$$\tilde{\mu}_M = \begin{cases} |\Gamma_M|^{-1}, & \text{if } X \in \Gamma_M; \\ 0, & \text{otherwise} \end{cases} \tag{19}$$

then

$$S_{\mathrm{G}}(\tilde{\mu}_M) = \log|\Gamma_M| = S_{\mathrm{B}}(M). \tag{20}$$

This is essentially the case for the microcanonical ensemble since $\Gamma_E \simeq \Gamma_{M_{\mathrm{eq}}}$. 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 $S_{\mathrm{G}}(\mu)$ does not change in time. $S_{\mathrm{G}}(\mu)$ is therefore “useless” for such systems not in equilibrium, while $S_{\mathrm{B}}(M(X_t))$ captures the essence of typical macroscopic behavior. In particular it satisfies the second law of thermodynamics.

Figure 4: Boltzmann's grave in Zentralfriedhof, Vienna, with bust and entropy formula

Summary of Boltzmann’s Ideas (also Maxwell, Kelvin, . . .)

Time-asymmetric behavior as embodied 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) that what we observe are “typical” behaviors — not all imaginable ones. Common alternate explanations, such as those based on equating irreversible macroscopic behavior with ergodic or mixing properties of ensembles (probability distributions) already present for chaotic dynamical systems having only a few degrees of freedom or on the impossibility of having a truly isolated system, are either unnecessary, misguided or misleading.

Let me end this section on systems described by classical mechanics by quoting Einstein's 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 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

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? 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 the microstate of a macroscopic system with an energy in a narrow interval $(E, E + \Delta E)$ to be a wave function $\psi \in \mathscr{H}_E$, where $\mathscr{H}_E$ is a shell in Hilbert space of thickness ΔE, i.e. $\mathscr{H}_E$ 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 $\mathscr{H}_E$ 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 $\Gamma_{M_{\mathrm{eq}}}$.

Following von Neumann[8], 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.

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[8] Chapter 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 $\mathscr{H}_E$. Their joint spectral decomposition defines an orthogonal decomposition

$$\mathscr{H}_E = \bigoplus_{\nu} \mathscr{H}_{\nu}, \tag{21}$$

Each subspace $\mathscr{H}_{\nu}$ consists of all linear combinations of the joint eigenvectors of the macro-observables whose eigenvalues lie in a narrow range. These subspaces $\mathscr{H}_{\nu}$ correspond to the different macrostates and the orthogonal decomposition (21) of $\mathscr{H}_E$ 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 $\mathscr{H}_\nu$, i.e.

$$\langle\psi|P_\nu|\psi\rangle \geq 1-\delta, \quad \delta \ll 1, \tag{22}$$

with P_ν being the projection to $\mathscr{H}_\nu$.

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 function is a complete description[9]. 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.

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[9] Be87,Go98

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

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

$$\frac{\dim \mathscr{H}_{\mathrm{eq}}}{\dim \mathscr{H}_E} = 1 - \varepsilon \tag{23}$$

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 $\mathscr{H}_\nu$;

$$S_{\mathrm{B}}(M_\nu) = \log d_\nu. \tag{24}$$

Given this correspondence between partitioning Γ_E and decomposing $\mathscr{H}_E$ most everything we said about isolated classical macroscopic systems then also holds for quantum systems. In particular for $\varepsilon \ll \delta$, most $\psi \in \mathscr{H}_E$ 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 case[10].

When I say "most ψ", I mean with respect to a uniform measure on the unit sphere in $\mathscr{H}_E$. This measure on "wave functions" was considered already by Schrödinger and particularly by Felix Bloch[11]. It yields the microcanonical density matrix ρ^{mc} but goes beyond it, in ascribing probabilities to any subset of $\mathscr{H}_E$.

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[10] Gr94

[11] Go06

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

$$\rho_S^\psi = \mathrm{tr}_{S^c} |\psi\rangle\langle\psi| \tag{25}$$

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

We can now define[12] 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 $\ell < \ell_0$, for an appropriate ℓ_0, the reduced density matrix of S is close to the thermal equilibrium density matrix of S

$$\rho_S^{\psi} \approx \rho_S^{\mathrm{mc}}, \tag{26}$$

$$\rho_S^{\mathrm{mc}} = \mathrm{tr}_{S^{\mathrm{c}}}\, \rho^{\mathrm{mc}}, \tag{27}$$

where ρ^{mc} is the microcanonical density matrix corresponding to a uniform distribution over energy eigenstates in $\mathscr{H}_E$. 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.

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[12] Go17

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

$$\frac{1}{D}\sum_{n=1}^{D}\langle n|P_{\nu_{\mathrm{eq}}}|n\rangle = \frac{1}{D}\,\mathrm{tr}(P_{\nu_{\mathrm{eq}}}) = 1-\varepsilon \tag{28}$$

Noting that $\langle n|P_{\nu_{\mathrm{eq}}}|n\rangle \leq 1$, the average being close to 1 means that most eigenstates are close to $\mathscr{H}_{\nu_{\mathrm{eq}}}$. 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. Then[13] 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 $\mathscr{H}_E \subset \mathscr{H}_1 \otimes \mathscr{H}_2$ be an energy shell. Then for most $\psi \in \mathscr{H}_E$ with $||\psi|| = 1$,

$$\operatorname{tr}_2 |\psi\rangle\langle\psi| \approx \operatorname{tr}_2 \rho^{\mathrm{mc}}, \tag{29}$$

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

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

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[13] Go06,Le08

The theorem says that most wave functions in the energy shell $\mathscr{H}_E$ 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 $\mathscr{H}_E$ are in MATE, then every state $\psi \in \mathscr{H}_E$ will sooner or later reach MATE and spend most of the time in MATE in the long run. That is because, writing $\overline{f(t)} = \lim_{T\to\infty} \frac{1}{T}\int_0^T f(t)\mathrm{d}t$ for time averages, $|n\rangle$ for the energy eigenstate with eigenvalue E_n and $\psi_t = e^{-iHt}\psi$,

$$\overline{\langle\psi_t|P_{\mathrm{eq}}|\psi_t\rangle} = \sum_{n,n'}\langle\psi|n\rangle\overline{e^{iE_nt}\langle n|P_{\mathrm{eq}}|n'\rangle e^{-iE_{n'}t}}\langle n'|\psi\rangle \tag{30}$$

$$= \sum_n |\langle\psi|n\rangle|^2\langle n|P_{\mathrm{eq}}|n\rangle \geq \sum_n |\langle\psi|n\rangle|^2(1-\delta) \tag{31}$$

$$= 1-\delta, \tag{32}$$

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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