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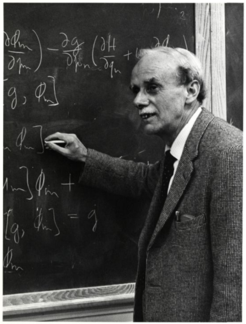

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Boltzmann's Entropy for Macroscopic Systems: An Overview

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Abstract[1]

Bolzmann's entropy is defined for individual macroscopic systems in a specified macrostate; equillibirum 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) the fact that 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.

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

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]

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[2] Ei49

Boltzmann's great insight was, as Einstein writes, to identify the entropy of an individual macroscopic system, in some micro-state X, with the log of the "number" of X's giving rise to the macro-state $M = M(X)$.

I will denote that set of X's by Γ_M and their "number" for a given M by $|\Gamma_M|$

When the system has an energy $H(X)$ in an interval $(E, E + \Delta E)$, $|\Gamma_M|$ is proportional to the "probability", with respect to the uniform (micro-canonical) measure, of finding the system in the macro-state M.

Boltzmann further noted that, for macroscopic systems, $|\Gamma_M|$ depends strongly on how close M is to M_{eq}, the equilibrium macrostate at energy E, with $\Gamma_{M_{\mathrm{eq}}}$ occupying almost the whole energy shell Γ_E. As I will argue, setting $\log|\Gamma_M|$ equal to the entropy $S_B(X)$ of a system in the macrostate $M = M(X)$ explains the observed entropy increase and approach to equilibrium in the time evolution of isolated macroscopic systems: the overwhelming majority of microstates $X \in \Gamma_M$, in a nonequilibrium macrostate M will evolve towards the equilibrium macrostate.

See Figure 1 for a representation of this.

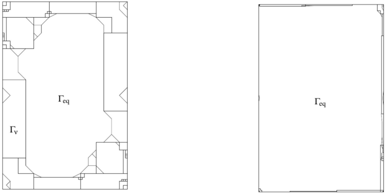

Figure 1: Schematic picture of the decomposition of the energy shell Γ_E. Here $\Gamma_{\mathrm{eq}} \equiv \Gamma_{M_{\mathrm{eq}}}$.

For classical systems the Γ_M are regions in the energy shell with sizes proportional to their Liouville volume. For quantum systems they are orthogonal subspaces of the system's Hilbert space with sizes proportional to their dimension.

The second picture is slightly more faithful. The actual ratio of the sizes is of order 2^N where N is the number of particles in the system. Let me describe this further for classical 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,

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

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 $H(X) = E$. We can take $H(X)$ to be of the form

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

with rapidly decaying $u(r)$.

Macrostates

To describe the macroscopic state of such a system, M, we specify an n-tuple of macrovariables $M(X) = \{M_1(X), M_2(X), \ldots, M_n(X)\}$, with resolution $\Delta M = \{\Delta M_j\}$. The macrostates then partition the energy shell into sets Γ_M of the form:

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

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 shown that for all "reasonable" choices of M, e.g. dividing up the box V into small regions and specifying, with some tolerances, the particle, momentum and energy densities in each region of V, 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 M is called the equilibrium macrostate M_{eq},

$$\frac{|\Gamma_{M_{\mathrm{eq}}}|}{|\Gamma_E|} = 1 - \varepsilon \tag{3}$$

with $\varepsilon \ll 1$, and $|\Gamma_M|$ the Liouville volume of Γ_M. The existence of a macrostate satisfying (3) is essentially a consequence of the law of large numbers.

A system in a microstate X is then in macroscopic thermal equilibrium if and only if $X \in \Gamma_{M_{\mathrm{eq}}}$.

The fact that $|\Gamma_{M_{\mathrm{eq}}}| \simeq |\Gamma_E|$ explains why one can use the microcanonical ensemble to compute properties of an equilibrium system despite the fact that Γ_E contains also nonequilibrium states with energy E. Their contribution is negligible when $N \gg 1$. This is independent of whether or not the dynamics is ergodic in a mathematical sense. In particular it is also true for ideal gases.

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 t 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, $M \neq M_{\mathrm{eq}}$, and are kept (effectively) isolated afterwards, is "typical" with respect to the micro-canonical measure restricted to Γ_M.

Boltzmann's Entropy

In other words, the vast majority of microstates in Γ_M (not all) will evolve in such a way that

$$S_{\mathrm{B}}(X) = \log |\Gamma_{M(X)}| = S_{\mathrm{B}}(M(X)) \tag{4}$$

will increase with time when $M(X_{t_0}) \neq M_{\mathrm{eq}}$. This explains the microscopic origin of the second law for individual macroscopic systems. $S_B(X_t)$ will increase until $X(t)$ reaches $\Gamma_{M_{\mathrm{eq}}}$ where it will stay for a very, very long time and its entropy will be given by

$$S_{\mathrm{B}}(M_{\mathrm{eq}}) = \log |\Gamma_{M_{\mathrm{eq}}}| \simeq \log |\Gamma_E| \tag{5}$$

its maximum possible value.

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

Boltzmann's heuristic argument for the non-decrease of entropy, based on relative phase space volume is, as Einstein says, the correct explanation for the asymmetric behavior typically observed in actual macroscopic systems. It is, however, very far from a mathematical proof.

A proof would be provided by the rigorous derivation from the microscopic dynamics of the kinetic and hydrodynamic equations such as the heat equation, Navier-Stokes equations, etc. 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.

Initial Conditions

The derivation answers the obvious question: How can we obtain time asymmetric equations for the typical behavior of macroscopic systems despite the time symmetry of the microscopic dynamics?

It is due to initial conditions. That is, starting out at some time t_1 with a nonequilibrium system in a macro-state $M \neq M_{\mathrm{eq}}$, and keeping the system isolated for $t > t_1$, then for X typical of Γ_{M_1}, $X(t)$ will evolve to Γ_{M_t}, such that $|\Gamma_{M_t}| \geq |\Gamma_{M_{t'}}|$ for times t' greater than $t \geq t_1$.

This is completely consistent with the fact that if we reversed all velocities at $t > t_1$, X_t would return to Γ_{M_1}.

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. Boltzmann[3]

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[3] 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."*
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> — R.P. Feynman[4]

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[4] Fe67

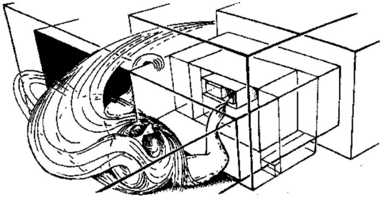

Figure 2: "Creation of the universe: a fanciful description! The Creator's pin has to find a tiny box, just 1 part in $10^{10^{123}}$ of the entire phase-space volume, in order to create a universe with as special a Big Bang as we actually find." from R. Penrose, *The Emperor's New Mind*

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

$$S_\mu \equiv - \int_\Gamma \mu \log \mu \, \mathrm{d}X. \tag{6}$$

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

$$\tilde{\mu}_M = \begin{cases} |\Gamma_M|^{-1}, & \text{if } X \in \Gamma_M; \\ 0, & \text{otherwise} \end{cases} \tag{7}$$

then

$$S_{\mathrm{G}}(\tilde{\mu}_M) = \log |\Gamma_M| = S_{\mathrm{B}}(M). \tag{8}$$

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 to leading order in N 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 3: Boltzmann's grave in Zentralfriedhof, Vienna, with bust and entropy formula