Boltzmann's Entropy for Macroscopic Systems: with Illustration from the Dilute Gas

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Abstract

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. This will be illustrated for a classical dilute gas.

(Much of this work was done jointly with S. Goldstein.)

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***."*[1]

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[1] 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 the entropy $S_B(X)$ of a system in the macrostate $M = M(X)$ equal to $\log|\Gamma_M|$ 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.

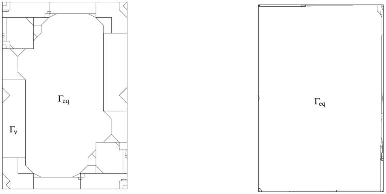

Figure 1: Schematic picture of the decomposition of the energy shell Γ_E. Here $\Gamma_{\rm eq} \equiv \Gamma_{M_{\rm eq}}$.

For classical systems the Γ_M are regions in the energy shell with sizes proportional to their Liouville volume.

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,

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

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 $H(X) = E$. 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 the values of 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, as already noted, 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}, and has the property that,

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

with $\varepsilon \ll 1$, and $|\Gamma_E|$ the Liouville volume of Γ_E. 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

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

will <u>increase with time</u> 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 <u>very, very</u> 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.

Note that while $S_B(X)$ may depend on the choice of the macrostate M, the equilibrium thermodynamic entropy obtained for $X \in \Gamma_{M_{\mathrm{eq}}}$ is, to leading order in the size of the system, independent of the choice of M. (This will be discussed more later.)

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 time 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[2] in 1973. (I particularly recommend his 1976 paper.)

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[2] La 75, 76

Initial Conditions

Lanford's 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 $M_1 \neq M_{\mathrm{eq}}$, 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}, after a time interval $t_1 - t$.

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."*

— R.P. Feynman[4]

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[4] Fe67

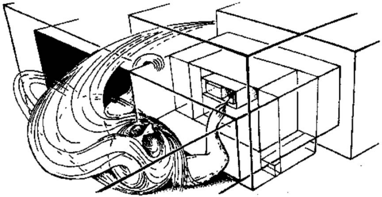

Figure 2: “Creation of the universe: a fanciful description! The Creator’s pin has to find a tiny box, just 1 part in $10^{10^{123}}$ of the entire phase-space volume, in order to create a universe with as special a Big Bang as we actually find.” from R. Penrose, *The Emperor’s New Mind*

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

Let me now turn to an illustrative example of the time evolution of $S_B(M)$ for a dilute gas system. Going beyond the hydrodynamical variables based on dividing $V \subset \mathbb{R}^d$ into cells we will use a more refined description of macrostates. To do that we note that for a system of N particles in a box V the microstate $X = \{\mathbf{r}_i, \mathbf{v}_i\}$, $i = 1, \ldots, N$, can be described as a set of N points in six (2d) dimensional one particle space,

$$X \leftrightarrow \sum_{i=1}^{N} \delta(\mathbf{x} - \mathbf{r}_i)\delta(\mathbf{v} - \mathbf{v}_i), \quad \mathbf{x} \in V, \mathbf{v} \in \mathbb{R}^d. \tag{9}$$

The Boltzmann Entropy for Dilute Gases

Dividing up this one particle space into cells Δ_α, $\alpha = 1, \cdots, n$, centered on $(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$, of volume $|\Delta_\alpha|$, we can, following Boltzmann, 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

$$f_\alpha |\Delta_\alpha| = N_\alpha / N \cong \int_{\Delta_\alpha} f(\mathbf{x}, \mathbf{v}) \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{v}. \tag{10}$$

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,

$$S_{\mathrm{B}}(f) = S_{\mathrm{B}}(M_f) = \log |\Gamma_{M_f}| \tag{11}$$

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

$$s_{\mathrm{B}}(f) = \frac{1}{N} S_{\mathrm{B}}(f) = -\sum |\Delta_\alpha| f_\alpha \log f_\alpha + \mathrm{const} \tag{12}$$

Boltzmann approximated (12), for small $|\Delta_\alpha|$, by setting

$$s_{\mathrm{gas}}(f) \cong -\int_V \mathrm{d}\mathbf{x} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{v}\ f(\mathbf{x},\mathbf{v}) \log f(\mathbf{x},\mathbf{v}) + \text{const.} \tag{13}$$

The maximum of $s_{\mathrm{gas}}(f)$ 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 obtained for the Maxwell distribution,

$$f_{\mathrm{eq}} = \rho(2\pi kT/m)^{-3/2}\exp[-m\mathbf{v}^2/2kT] \tag{14}$$

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

In this case $\Gamma_{M_{f_{\mathrm{eq}}}} = \Gamma_{M_{\mathrm{eq}}}$ and the equilibrium entropy per particle for a dilute gas is given, to leading order in the size of the system, by

$$s_{\mathrm{gas}}(f_{\mathsf{eq}}) = \frac{3}{2}\log T - \log\rho + \mathrm{Const.} \tag{15}$$

the same as the equilibrium Clausius entropy $S_{\mathsf{eq}}(E, N, V)$ per particle for a dilute gas, with density ρ.

Consider now the time evolution of the entropy of a dilute gas when its volume is expanded by lifting a constraint. We shall see that replacing the sum (12) by the integral (13) may not be valid when the system is in a nonequilibrium nonuniform state.

Before doing that let me discuss briefly Lanford's derivation of the Boltzmann Equation. (This is like "bringing coal to Newcastle" for this audience). In this derivation the meaning of a smooth f is made precise.

My emphasis, like Lanford's, is on individual macroscopic systems. In the works by Bodineau, et al.[5], they start with a probability measure which is close to a product of smooth one particle distributions $f(x, v)$. They prove that $f(x, v, t)$ describes typical behavior of individual systems and go beyond that to consider fluctuations and large deviations.

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[5] Bo23

Lanford's Theorem

Consider a gas consisting of N hard balls 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 the Boltzmann-Grad (BG) limit: b^{-1} is proportional to the mean-free-path between collisions.

Choose now a smooth $f_0(x, v)$ and as N increases consider microstates $X_N \subset \Gamma_{M_{f_0}}$ such that the fraction of particles in cubical boxes Δ_α is required to satisfy (10) ever more closely, with equality in the BG limit,

$$\lim_{\mathrm{BG}} N_\alpha(X_N)/N = \int_{\Delta_\alpha} f_0(\mathbf{x}, \mathbf{v}) \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{v}. \tag{16}$$

N.B. The BG limit is required for (16) 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):

A typical microstate $X_N(0) \in \Gamma_{M_{f_0}}$ will evolve, via the Hamiltonian dynamics, to a microstate $X_N(t)$ such that, in the BG limit

$$\frac{N_\alpha(X_N(t))}{N} = \int_{\Delta_\alpha} f(\mathbf{x}, \mathbf{v}, t) \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{v} \tag{17}$$

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

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{x}} = bQ(f, f) \tag{18}$$

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

The BE gives a deterministic evolution from the macrostate M_{f_0} to the macrostate M_{f_t} in the BG limit. It describes approximately the evolution of the coarse grained empirical distribution for a dilute gas. For extensions see [Bo23].

The second law generalized to nonequilibrium macrostates now says that for a *typical* microstate of a dilute gas with $X(0) \in \Gamma_{M_{f_0}}$, $X(t) = T_t X(0) \in \Gamma_{M_{f_t}}$, the entropy will be non-decreasing with t.

This is exactly what happens for $s_{\mathrm{gas}}(f_t)$ defined in (13) for f_t evolving according to the Boltzmann equation:

Boltzmann's $\mathcal{H}$-theorem :

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} s_{\mathrm{gas}}(f_t) &= \frac{\mathrm{d}}{\mathrm{d}t} \left\{ - \int_V \mathrm{d}\mathbf{x} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{v}\ f_t(\mathbf{x},\mathbf{v}) \log f_t(\mathbf{x},\mathbf{v}) \right\} \\ &= b\mathcal{I}(f_t) \geq 0. \end{aligned} \tag{19}$$

As put by Boltzmann[6]:

> *"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."*

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[6] Bo98

We note that the rate of increase of entropy in (19) is proportional to $b = \lim_{\mathrm{BG}} Nd^2$. If one takes the limit $N \to \infty$, $d \to 0$ in such a way that $Nd^2 \to 0$ then $b = 0$ and the time derivative of $s_{\text{gas}}(f)$ given in (19) is equal to zero.

The reason for this lack of change in $s_{\mathrm{gas}}(f)$ when $b = 0$ is that $s_{\mathrm{gas}}(f)$, defined in terms of a smooth $f(x, v, t)$ does not capture all the features of the evolution of macrostates, defined in terms of coarse graining, $|\Delta_\alpha| > 0$. Keeping $|\Delta_\alpha| > 0$ is essential for seeing the increase of the Boltzmann entropy from spreading in physical space.

To see the increase of $s_{\mathrm{B}}(M_f)$ when $b=0$ Chakraborti et al. investigated numerically the time evolution of a spatially nonuniform ideal gas in one dimension[7]. They started the system in a microstate X randomly chosen from $\Gamma_{M_{\text{eq}}}$ of a system of N particles confined to an interval of length L, and then, let the gas expand to an interval of length $2L$. They chose cells Δ_α all of equal size $\Delta = |\Delta x||\Delta v|$ with cutoff on the maximal speed $|v|$). They computed the change in

$$s_{\mathrm{B}}^f(t) = \frac{1}{N} S_{\mathrm{B}}(M_f) = \sum_\alpha |\Delta_\alpha| f_\alpha \log f_\alpha + \text{Const} \tag{20}$$

as this system evolved in time without any collisions, see also[8].

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[7] [Ch21]

[8] [Ch23]

We found, to our surprise, that the time "$t_{\rm eq}$" it took the system with initial entropy $S_{\mathsf{eq}}(L)$ to reach the new entropy, $S_{\mathsf{eq}}(2L) = S_{\mathsf{eq}}(L) + N \log 2$, depended strongly on the width $|\Delta v|$ of the single-particle phase space cells used to define the macrostate M_f and thus the Boltzmann entropy $S_B(M_f)$. The smaller $|\Delta v|$, the slower the entropy production, see Fig. 4.

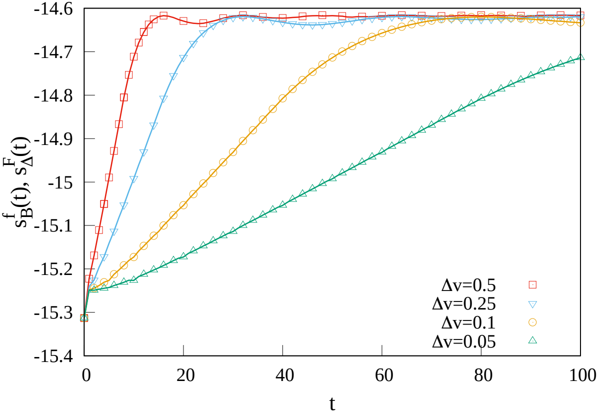

Figure 4: The time evolution of $s_{\mathrm{B}}^{f}(t)$ when X_0 is chosen at random from an initial Γ_{M_0} corresponding to the phase space region where all N particles are in the left half of the box with energy $E \simeq N\epsilon_0$, $\epsilon_0 = 1.25$ corresponding to a temperature 2.5, $N = 10^7$. (The continuous line $s_{\Delta}^{F}(t)$. will be explained later.)

The reason for this strong dependence on $|\Delta v|$ is that for the ideal gas the only mechanism for uniformizing the velocity distribution over all of space is via the difference between the total distance traveled in a time t by the particles with velocity v versus those with velocity $v + \Delta v$. In order for the systems to approach equilibrium, this distance must exceed L, which only occurs after time $t_{\text{eq}} \sim L/|\Delta v|$.

The time evolution of the entropy is much less sensitive to the spatial size Δx of the cells. The time scale for the initial uniformization of the spatial density (ignoring the local velocity distributions) is of order L/v_{th}, where v_{th} is the mean speed, this time is much shorter than t_{eq}. It accounts for the apparent jump in s at $t = 0$.

The different curves $s^f_{\mathrm{B}}(t)$ collapse to a single curve when t is rescaled as $t = \frac{2L\tau}{|\Delta v|}$, where $2L$ is the circumference of the circle to which our system can be mapped.

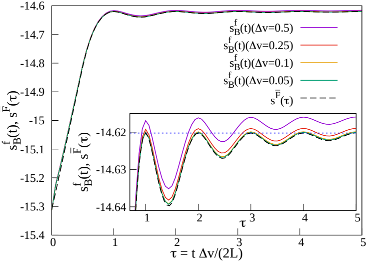

Figure 5: The figure shows a collapse of the data presented in the previous figure for different values of Δv, on plotting the entropy as a function of the scaled time $\tau = t\Delta v/(2L)$. The dashed line in the insert is the graph of $s^{\overline{F}}(\tau)$, will be defined defined below. The oscillations have period 1 with maxima at $\tau = 1, 2, \ldots$, the time it takes "Δv" to go around the circle.

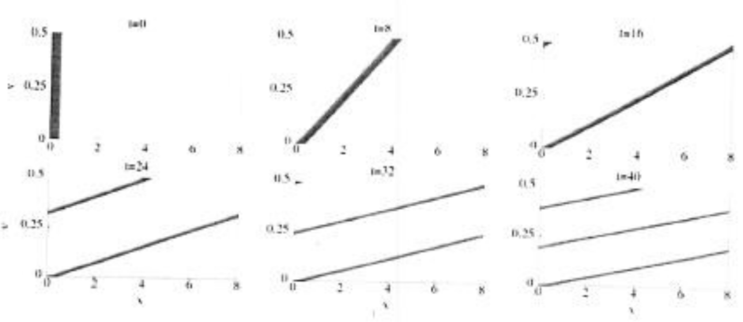

Figure 6: Plot showing the evolution of one of the boxes used earlier, $N = 10^6$ particles, in the (x, v) plane, where the particles move on a circle of length $2L = 8$. The particles were initially distributed uniformly in a small box with $\Delta x = 0.25$, $\Delta v = 0.5$. With time the box gets continually stretched and, at times that are multiples of $2L/\Delta v = 16$, the stretched pieces wind completely around the box. Comparing with Fig 5 we see that the maxima in $s_B^f(t)$ occur at times $\approx 16, 32$, at which the winding around the length $2L$ is complete. [Ch21]

To study analytically the curves in Figures 4 and 5 [Ch21] define

$$F(x, v, 0) = \sum_{i=1}^{N} \langle \delta(x - r_i) \delta(v - v_i) \rangle, \tag{21}$$

where the average is over the $\{r_i, v_i\}$ in canonical distribution (equivalent to the microcanonical one with the same energy) for the given density and temperature. We then evolve F according to Eq. (18) with $b = 0$, $F(x, v, t) = F(x - vt, v, 0)$, periodic over the circle. We then integrate $F(x, v, t)$ over cells Δ_α to obtain a an averaged N_α and thus the entropy $s_\Delta^F(t)$. This is plotted as a continuous line in Fig4. We see in the figure that $s_\Delta^F(t)$ coincides with $s_{\mathrm{B}}^f(t)$, the entropy computed for a single typical microstate.

Taking the limit $|\Delta_\alpha| \to 0$ we obtain $s^{\overline{F}}(\tau)$ given by

$$s^{\overline{F}}(\tau) = -\frac{1}{N}\int \overline{F}(x,v,\tau)\ln \overline{F}(x,v,\tau)dxdv \tag{22}$$

where

$$\overline{F}(x,v,\tau) = \frac{1}{2L\tau}\int_0^{2L\tau} F(x-x',v,0)dx'. \tag{23}$$

Setting

$$F(x,v,0) = \rho \mathrm{h}(v)[1+\phi(x,v)], \quad \text{with } 2L = 1 \tag{24}$$

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

we obtain

$$\begin{aligned} \overline{F}(x,v) &= \rho \mathrm{h}(v)[1+\frac{1}{\tau}\int_0^\tau \phi(x-x',v)dx'] \\ &= \rho \mathrm{h}(v)[1+\frac{1}{\tau}\psi(x,v,\tau)], \end{aligned} \tag{25}$$

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

$$\psi(x,v,n) = 0, \qquad \text{for } n = 1,2,3,\ldots. \tag{26}$$

This yields the $s^{\overline{F}}(\tau)$ plotted in the insert of Figure 5 for the initial condition used. The maxima, all of equal height, occur at $\tau = 1,2,\ldots$.

Time evolution of the Boltzmann entropy for hard discs

To elucidate the time evolution of $S_B(M)$ for different choices of $|\Delta_\alpha|$ when the interaction between the particles is not neglected but the mean free path is still large comparable to the scale of the spatial inhomogeneity Garrido et al. have carried out molecular dynamics computations for the time evolutions of a two-dimensional system of N hard discs[9].

The system is started in a microstate X chosen at random from a canonical Gibbs ensemble with temperature $T = 1$ (setting $K_B = 1$) in a rectangular box of size $L_x = 1/2$, $L_y = 1$ with periodic boundary conditions along the y direction and hard walls constraining the system along the x direction. The disc's radius r is fixed in such a way that the system has a given initial areal density $\eta = \pi r^2 N/|V|$ where $V = L_x L_y = 1/2$. The corresponding mean free path when the system is dilute is $\lambda \sim (\eta N)^{-1/2}$.

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[9] P. Garrido, S. Goldstein, D. Huse and J.L.L (in preparation

At time $t = 0$ we remove the hard walls and let this gas of discs expand to a box of size $L_x = L_y = L = 1$ with now periodic boundary conditions along both directions. We study the time evolution of this system until it reaches an equilibrium state $X \in \Gamma_{M_{\mathrm{eq}}}$ in this larger periodic box.

The degrees of freedom associated with y and v_y, along which direction the system does not expand, remain near thermal equilibrium. Therefore the Boltzmann entropy associated with these y, v_y degrees of freedom remains approximately constant in time while the system expands along the x direction and approaches the new thermal equilibrium.

We will consider only the entropy due to the degrees of freedom associated with x and v_x, since it is this part of the entropy that is most out of equilibrium and changing with time.

Thus we divide the four-dimensional one-particle phase space $(x, v_x; y, v_y)$ into cells Δ_α of extent Δx and Δv_x in the (x, v_x) plane with each cell including the full range of y and v_y. We count $N_\alpha(t)$, the number of particles in Δ_α at time t and evaluate the

$$s(t; \Delta, N, \eta) = -\frac{\Delta}{N} \sum_\alpha \frac{N_\alpha(t)}{\Delta} \log \frac{N_\alpha(t)}{\Delta}. \tag{27}$$

All cells have equal "area" $|\Delta_\alpha| = |\Delta x||\Delta v_x| = \Delta$ in the (x, v_x) plane.

Results for different values of the mean free path λ:

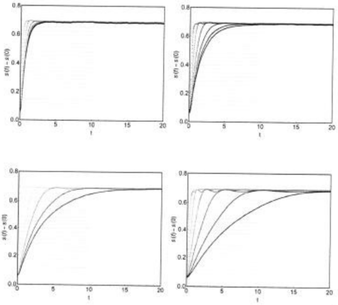

Figure 7: Boltzmann entropy for $N = 10^5$ and areal densities $\eta = 10^{-6}$ (upper left), $\eta = 10^{-7}$ (upper right), $\eta = 10^{-8}$ (lower left) and $\eta = 10^{-9}$ (lower right) for 16 cells along the x direction and different values of Δv_x.

The mfp for the different boxes are $\lambda \approx .7$, $\lambda \approx 2.2$, $\lambda \approx 5$, $\lambda \approx 22$. For $\lambda \approx 22$ the dependence on $|\Delta v_x|$ is the same as for the ideal gas, $\lambda = \infty$, while for $\lambda = .7$ there is almost no dependence on $|\Delta v_x|$. It is this latter case for which $s_{\text{gas}}(f)$ is a good approximation to the entropy of the dilute gas. This is surely what Boltzmann had in mind.

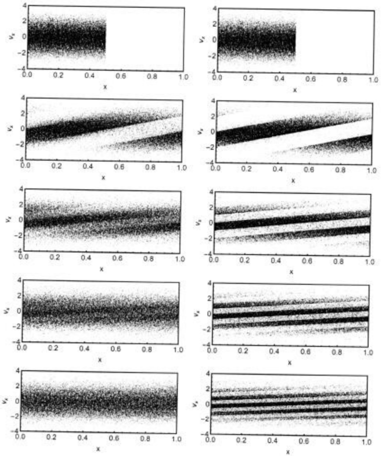

Figure 8: (x, v_x)-phase space typical evolution of a system in the x, v_x plane with $N = 10^5$ discs with areal densities $\eta = 10^{-4}$ (left column) and $\eta = 10^{-6}$ (right column) for times (from top to bottom) t =0.0, 0.5, 1.0, 1.50 and 2.0.

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. Parris[10]. 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 and a "smooth" velocity distribution, say Maxwellian with variance 1.

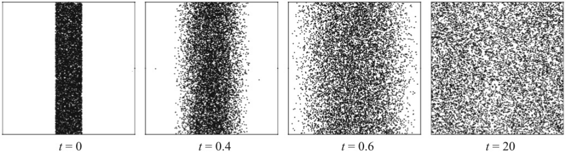

Figure 9: (From BP) Numerical simulation of the free expansion on the 2-torus of a non-interacting gas of 10^4 particles having a thermal distribution of momenta with mean thermal speed equal to unity, initially confined in the horizontal direction to the region $0.4 < x < 0.6$, at the sequence of times indicated.

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[10] BiPa17

To define the macro state M_f BP divide the unit torus into $\mathscr{L}$ squares, D_j, $j = 1, \ldots, \mathscr{L}$, 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 $\mathscr{L}$ 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. will 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 $\Gamma_{M_{t_1}} = \Gamma_{M_1}$, 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].

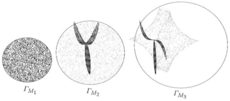

Figure 10: Time evolution of Γ_{M_1}

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[11] $\frac{\mathrm{d}}{\mathrm{d}t} S_{\mathrm{B}}(M_t) \geq 0$, exactly what Boltzmann showed for the BE.

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[11] 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 $|\Gamma_{M_{t'}}| \geq |\Gamma_{M_2}|$.

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