On the Time Evolution of Macroscopic Systems

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0. Preface

The problems of non-equilibrium statistical mechanics, philosophical, mathematical and practical have always been, and continue to be, close to Harold Grad's heart. Our choice of words here is deliberate – anyone who has talked to Harold about irreversibility knows the passion which he brings to bear on the search for understanding of this old problem which refuses to go away. This passionate caring has been a great inspiration to us as we are sure it has been to many others. It has also been a strong incentive to keep us honest. For woe to him or her who tries to use muddled arguments. Claims of a "derivation" of the Boltzmann equation without the use of proper limit procedures are swiftly shown to be fallacious. Persistent sinners are consigned to a place where the "ten common errors" of such derivations perpetually flash on and off in blinding neon lights.

Conceptual clarity embodied in logical precision has always been Harold's guideline. He showed this from the beginning in elucidating the limit in which one might hope to *prove* the Boltzmann equation, the famous Boltzmann–Grad limit [1]. While we are still far from completely carrying out Grad's program of an exact derivation of kinetic equations, there has been some progress in recent years. We shall describe here some of these results as they refer to a simple model system. We believe that despite its simplicity this model contains many essential features of the observed irreversible behavior of general macroscopic systems. We hope that our explanations will not be found too defective by Harold Grad to whom this article is dedicated with affection and appreciation.

1. Introduction

We restrict ourselves here to one of the simplest non-equilibrium processes, that of self-diffusion. This avoids many technical problems and enables us to

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focus on the central issues. It is certainly the case for which one can *prove* the most results at the present time.

To describe self-diffusion we consider a binary mixture of fluids in which the two components are mechanically identical but are distinguished by labels which remain unchanged in the course of time. Such a system can be realized by a fluid of uncharged particles with nuclear spin $\frac{1}{2}$ interacting through spin-independent forces: a situation which exists to an excellent approximation in liquid He^3 (cf. [2]). Within our classical model we may simply imagine that each particle carries a color, either black or white, and that they interact as hard spheres.

Consider now the situation illustrated in Figure 1. We have a box Λ of width 10 cm and length 20 cm divided into two equal parts. There are altogether

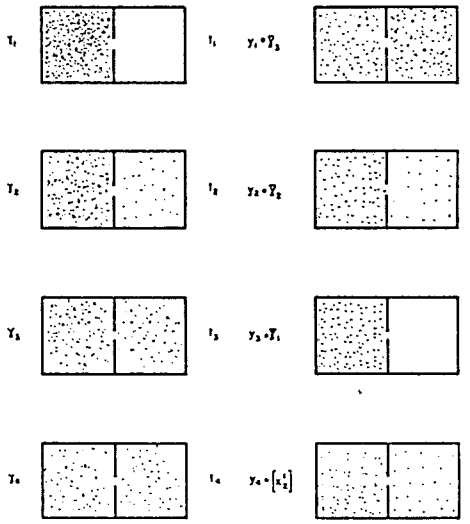

Figure 1 Time evolution of color density in "real" (left column) and "velocity reversed" case (right column) – see text.

$\frac{1}{2}N \cong 10^{20}$ black and $\frac{1}{2}N$ white atoms in the box of which only the black are visible. The macroscopic experiment or observation consists in determining the numbers $N_1(t)$ and $N_2(t)$ of black particles in the left and right parts, Λ_1 and Λ_2, at time t: $N_1(t)+N_2(t)=\frac{1}{2}N$. Consider first the left side of the figure. The sequence illustrated represents a macroscopic experiment carried out as follows: we start with the box divided by a thin partition and fill the left part Λ_1 with a gas of black particles, and the right side with a gas of white particles both at room temperature and 0.01 atmospheric pressure. We then wait for a few minutes and at time $t=t_1$, the beginning of our observations, we remove the partition. The configurations of black particles shown in the left-hand column of Figure 1 are our imagined ones at the observation times t_j, $j=1,2,3,4$; no surprise

here as long as we tell you that $t_1 < t_2 < t_3 < t_4$. The system goes from a highly non-uniform color density to a uniform one: precisely the kind of behavior we are used to seeing in such experiments. (For He^3 one applies initially a strong magnetic field, up in Λ_1 and down in Λ_2, and then measures the magnetization.)

We are sure the reader will agree that these imagined observations are consistent with Hamilton's equations of motion for a system of particles interacting with a Lennard-Jones or hard-core pair potential. It is also true, and consistent with the macroscopic equations of motion, that the evolution of the density, kinetic energy and other similar quantities can be described *for the times considered* very accurately by irreversible kinetic equations, e.g., the appropriate (linear) Boltzmann equation and the hydrodynamic equations. What is *inconsistent* is to say that the behavior of the system will be accurately described by such kinetic equations in *all* situations we can imagine. Put differently, the kinetic equations may turn out to be very poor approximations for some initial states. For example, if we imagine that at time t_2 we somehow put our system in the state $R\gamma(t_2)$ obtained from the state $\gamma(t_2)$ by reversing all velocities, then for the time interval (t_2, t_3) we would not observe the color getting more uniform as would be predicted by the kinetic equations. What should happen in such a situation is shown on the right side of Figure 1 including, on top, the configuration corresponding to that state at t_1 which would give $R\gamma(t_2)$ at time t_2 *without further intervention.*

The appropriate questions are then of the following type: (i) For which initial dynamical states is the time evolution of the color density well approximated by a kinetic equation? (ii) Why do we apparently *always* find in nature and produce in the laboratory initial dynamical states whose time evolution is, over the times observed, well approximated by a kinetic equation?

The second question easily leads into cosmological considerations, i.e., "In what state was the universe created?" Many people believe that cosmological principles play an essential role in the understanding of irreversibility (cf. [3], [4]). We will be more earthbound here and try only to explain to what extent the first question can be answered. This will, to some extent, also shed light on the second question.

In describing the example we implicitly made some assumptions which we repeat for the sake of clarity. We assume that the dynamics of the particles is given by classical mechanics and that our system is completely isolated. We thus ignore the fact that atoms and molecules follow the laws of quantum mechanics and that, because of imperfect isolation, there are always external perturbations. It is our contention that these facts do not play an essential role in the *qualitative* understanding of irreversible behavior of macroscopic systems. More precisely, we believe that even in an entirely classical and idealized world, such as can *in principle* be produced by computer simulations of the dynamics of the system we just described (perhaps with a somewhat smaller N) "typical" pictures would look just as they do on the left in Figure 1, and we would also be able to produce

the pictures on the right. It is then this phenomenon of the color spreading out diffusively for "all" our computer generated "typical" initial states which is the subject of our study.

As the reader may have noticed we did not say what is a "typical" dynamical state. Unfortunately this was not an oversight. At present we do not have any criterion which would tell us whether a *given* state of particles will follow a macroscopic equation or not. In fact, we do not even have an idea what form such a criterion could possibly take. Instead we have to be satisfied with a purely *probabilistic* characterization of "exceptional" and "typical" dynamical states. It is at this stage that Statistical Mechanics enters. We look for and we exhibit an initial ensemble such that most (with respect to that ensemble) configurations follow the macroscopic equation. As a next step we shall show that this property is shared by a whole class of initial ensembles. (In a general context, this problem of the choice of the initial ensemble is one of the questions much emphasized by Grad [1], [5]. It is discussed in detail, although not entirely resolved, in a recent article by Penrose [6], which we recommend to you highly. That article also contains a discussion of various approaches to the problem of irreversibility and a very extensive list of references.) It is then in this spirit of statistical mechanical ensembles in which our discussion will proceed.

We shall discuss self-diffusion in two physically distinct situations: (i) *Low density regime*: Here the Boltzmann–Grad limit is the appropriate idealization of a dilute classical gas for which the Boltzmann equation ought to hold exactly. Grad's program (cf. [1]) for carrying out such a proof was carried out by Lanford [7] with a limitation to early times. Lanford's results applied to self-diffusion prove the validity of the kinetic description for all times. Our remarks are taken from our joint paper with van Beijeren and Lanford [8] and from [9]. (ii) *Finite density*: The finite density situation, while clear in principle, involves a difficult dynamical problem (cf. [10]). If our model is further simplified to the so-called Lorentz gas, then the results of Bunimovich and Sinai [11] apply. These are discussed in Section 5.

2. Self-Diffusion at Low Density and Lanford's Theorem

We consider a system of N hard spheres of diameter εd and unit mass inside the box Λ. These spheres are either black (≡colored) or white (≡colorless). They move freely until a collision whereupon they bounce off each other elastically. The spheres are specularly reflected at the wall. Their color does not change in the course of time. Ignoring their color the particles are assumed to be in thermal equilibrium. This means that the velocity distribution is Maxwellian at a given inverse temperature β and that the positions are distributed according to the normalized free-volume measure. Technically it will be slightly more convenient to use the grand-canonical ensemble with fugacity z.

Every particle configuration defines a discrete, normalized color distribution. One simply locates a δ-function with weight $1/N$ at the position of every black particle. On a macroscopic scale this discrete distribution is then approximated by a smooth one. This is certainly a very reasonable thing to do as long as one uses a grid which contains many particles in every unit cell. On the other hand, at a sufficiently fine scale the discrete structure of the color distribution will of necessity manifest itself. To ensure the validity of the macroscopic description in a precise way one is forced to pass to a *continuum limit* where the number of particles in every macroscopic region tends to infinity. (This continuum limit should be regarded as a first step with obvious improvements easily stated but hard to prove.) At low density the correct continuum limit is the *Boltzmann–Grad limit*. This limit is determined by letting $N \to \infty$, $\varepsilon \to 0$ with mean free path kept fixed which leads to

$$\varepsilon^2 N = \text{const.} \tag{1}$$

For the grand-canonical ensemble, which will be used exclusively in this paper, the corresponding condition is

$$\varepsilon \to 0, \quad z_\varepsilon = \varepsilon^{-2} z = \text{const.} \tag{2}$$

Note that the first density correction to any intensive thermodynamic property is proportional to $\varepsilon^{-2} z \times$ (volume of a sphere of diameter εd) $= O(\varepsilon)$, which vanishes as $\varepsilon \to 0$. Thermodynamically the system approximates, as $\varepsilon \to 0$, to an ideal gas in the following sense: If one picks a point q in Λ and a little ball with radius $\varepsilon^{2/3} R$ around it, where R is an arbitrary length, then the average number of particles within this ball is approximately independent of ε and their distribution, spatially blown up by a factor $\varepsilon^{-2/3}$, approaches that of an ideal gas (Poisson distribution) in a ball of radius R, in the limit $\varepsilon \to 0$.

We return now to the example discussed before. At $t = 0$ the particles in Λ_1 are black and those in Λ_2 are white. At low density the kinetic equation governing the evolution of a color profile is the *linear Boltzmann equation* which reads

$$\frac{\partial}{\partial t} f(q, v, t) = -v \frac{\partial}{\partial q} f(q, v, t) + z \int dv_1 \int_{\omega \cdot (v - v_1) \geq 0} d\omega \, \omega \cdot (v - v_1) \times \{h_\beta(v_1') f(q, v', t) - h_\beta(v_1) f(q, v, t)\}. \tag{3}$$

Here $f(q, v, t)$ is the density of black particles in one-particle phase space at time t, $h_\beta(v) = (\beta/2\pi)^{3/2} e^{-\beta v^2/2}$, ω is a unit vector, and the pre-collisional velocities (v', v_1') and the post-collisional velocities (v, v_1) are related by

$$v' = v - [\omega \cdot (v - v_1)]\omega,$$
$$v_1' = v_1 + [\omega \cdot (v - v_1)]\omega.$$

In our example the initial conditions are

$$f(q, v) = \chi_{\Lambda_1}(q) z h_\beta(v), \tag{4}$$

where χ_Δ is the characteristic function of the set Δ.

Microscopically, for every given ε we simply count the number of black particles, $N_1^\varepsilon(t)(N_2^\varepsilon(t))$, in $\Lambda_1(\Lambda_2)$ at time t. These are random variables. Their ε-dependence comes through the ε-dependence of the initial ensemble and of the dynamics. Since the fugacity increases like ε^{-2}, the typical magnitude of $N_1^\varepsilon(t)$ and $N_2^\varepsilon(t)$ are normally of the order ε^{-2}. Their distribution in the limit $\varepsilon \to 0$ follows from the following theorem, due to Lanford [7].

PROPOSITION 1.

$$\lim \varepsilon^2 N_{1(2)}^\varepsilon(t) = \int_{\Lambda_{1(2)}} dq \int_{R^3} dv \, f(q, v, t) \tag{5}$$

in probability, where $f(q, v, t)$ satisfies (3), *with initial condition* (4).

The *actual number* of black particles in Λ_1 and in Λ_2 can be predicted on the basis of the kinetic equation (3) in the following precise sense: If we give ourselves an (arbitrary) error bar δ, then for sufficiently small ε

$$\left| \varepsilon^2 N_1^\varepsilon(t) - \int_{\Lambda_1} dq \int_{R^3} dv \, f(q, v, t) \right| \leqq \delta \tag{6}$$

with the *exception* of a set of initial states with total weight *in the initial ensemble* less than δ. In our example the weight of a dynamical state, initially or at any other time, is given by the grand-canonical ensemble with fugacity $\varepsilon^{-2} z$.

In Proposition 1 we chose, for the sake of our example, to count the number of black particles in a very particular region of the one-particle phase space, namely, the region corresponding to the particle being located in the region Λ, of real space. This is not necessary. One can choose any Borel set Δ in one-particle phase space and count the number, $N^\varepsilon(\Delta, t)$, of black particles in Δ at time t. Then Proposition 1 is still valid in the sense that

$$\lim_{\varepsilon \to 0} \varepsilon^2 N^\varepsilon(\Delta, t) = \int_\Delta dq \, dv \, f(q, v, t) \tag{7}$$

in probability. Moreover, our initial condition (4) is very special; but the result also applies to more general initial conditions. This will be discussed in the following section.

Physically one would like to make observations not only at individual times, but also continuously. We would therefore like to prove a strengthened version of Proposition 1, such as

$$\lim_{\varepsilon \to 0} \text{Prob} \left\{ \sup_{0 \leq t \leq T} \left| \varepsilon^2 N^\varepsilon(\Delta, t) - \int_\Delta dq \, dv \, f(q, v, t) \right| > \delta \right\} = 0. \tag{8}$$

This result has *not* been proved so far. In fact, if T is replaced by ∞, then (8) is wrong because of the Poincaré recurrence, but presumably (8) will hold if T grows with some inverse power of ε.

Having discussed the Boltzmann–Grad limit in some detail we return to our original problem, namely to find a criterion for initial dynamical states for which the kinetic description is a good approximation. Proposition 1 states that at sufficiently small ε, the actual color profile is, for a large fraction of initial dynamical states, well approximated by the solution of the linear Boltzmann equation. Given a particular state we have, however, no way to tell whether the evolution of its color profile is governed by the kinetic equation or not. In that sense the characterization of "exceptional" configurations is purely probabilistic. Physically one would hope to have eventually a more mechanical, pointwise, characterization, but even its form is unclear at present.

Let us digress now to explain on an intuitive basis why Proposition 1 is valid. Given our initial condition, the average number of black particles at (q, v) at time t is equal precisely to the probability that a *particle* in the hard-sphere gas starting at $(q, -v)$ is in Λ_1 at time t. Similarly, the average number of pairs of black particles at (q_1, v_1) and (q_2, v_2) at time t equals the probability that two particles starting at $(q_1, -v_1)$ and $(q_2, -v_2)$ are both in Λ_1 at time t (disregarding here unessential equilibrium factors). For small ε, any given particle, call it a "test" particle, moves through a "dust" of gas particles. Starting at $t=0$ it collides for the first time after a roughly exponentially distributed waiting time. After the collision it takes another roughly exponentially distributed time to collide with a second gas particle, etc. The probability of colliding again with the same gas particle is of the order ε^2 and vanishes as $\varepsilon \to 0$. Consequently, the "stochastic" time evolution of a test particle becomes Markovian in the limit $\varepsilon \to 0$. The motions of two test particles are correlated either directly because they may collide with each other or indirectly because they may collide with the same gas particles. But again this is an effect of order ε^2 and their motions become independent in the limit. Translating these results back to $N_1^\varepsilon(t)$ shows then that the average of $\varepsilon^2 N_1^\varepsilon(t)$ is governed by the linear Boltzmann equation and that the variance of $\varepsilon^2 N_1^\varepsilon(t)$ tends to zero as $\varepsilon \to 0$.

3. Correlations in the Initial State

Once we accept a probabilistic characterization of "good" initial states, it is natural to ask how strong a correlation between mechanical and color degrees of freedom can be built into the initial state without invalidating Proposition 1. Let us denote by $x_j = (q_j, v_j)$ the position and velocity of the j-th particle and by σ_j its color, where $\sigma_j = 1$ stands for black and $\sigma_j = 0$ for white, and let $\rho_{eq,n}^{(z)}$ be the n-th correlation function of the grand-canonical ensemble at inverse temperature β and fugacity z. We always assume that the joint correlation functions

satisfy initially, and therefore at all times,

$$\sum_{\sigma_1=0,1} \cdots \sum_{\sigma_n=0,1} \rho_n(x_1, \sigma_1, \cdots, x_n, \sigma_n, t) = \rho_{eq,n}^{(z)}(x_1, \cdots, x_n). \tag{9}$$

Now, in our example, the initial state at $t=0$ corresponds to setting

$$\rho_n(x_1, \sigma_1, \cdots, x_n, \sigma_n) = \left\{ \prod_{j=1}^{n} g(q_j, \sigma_j) \right\} \rho_{eq,n}^{(z)}(x_1, \cdots, x_n),$$

with

$$g(q, \sigma) = \chi_{\Lambda_1}(q)\sigma + \chi_{\Lambda_2}(q)(1-\sigma). \tag{10}$$

Clearly, the factorization in (10) is a very special choice which is not preserved in the course of time. We would therefore like to consider more general initial conditions.

On the other hand, the invariance of the equations of motion under velocity reversal and $t \to -t$ shows that one cannot hope to allow, even under the constraint (9), arbitrary initial correlations: If we start the system in the state (10), reverse all the velocities at time t, and take the resulting state as our initial state, then the color profile of most (with respect to the velocity-reversed initial state) configurations does not at first follow the linear Boltzmann equation. In our example the purely mechanical correlations in the velocity-reversed state are still given by the grand-canonical ensemble, but the velocity reversal produces correlations between color and position and velocity of a type which render the kinetic equation invalid.

For self-diffusion the characterization of the allowed initial correlations can be taken from King's thesis [12]. To explain it we have to describe in some detail the convergence of the joint correlation functions in the Boltzmann–Grad limit. Let us consider the n-particle phase space $\Gamma_n = (\Lambda \times R^3)^n$. We denote by $s \to q_j(s)$ the *free* motion of the j-th particle taking into account the collisions with the wall. We define then the subset $\Gamma_n(t)^c$ of post-collisional configurations at time $t > 0$. A point $(q_1, v_1, \cdots, q_n, v_n)$ belongs to $\Gamma_n(t)^c$, if this phase point followed *backwards* in time with the *free time evolution* leads to a configuration in which a collision occurred within the time span t, i.e., if for some pair (i, j) we have $q_i(-s) = q_j(-s)$ with $0 \leqq s \leqq t$. (The analogous definition holds for negative times.) $\Gamma_n(t)^c$ is a set of Lebesgue measure zero, since the coincidence condition occurs only on certain hypersurfaces in Γ_n. We denote by $\Gamma_n(t) = \Gamma_n \backslash \Gamma_n(t)^c$ the complement of $\Gamma_n(t)^c$. Note that $\Gamma_n(t)$ is *not* invariant under velocity reversal. The precise condition on the initial state is then the following: We give ourselves a piecewise continuous color distribution $f(q, v, \sigma)$ such that

$$f(q, v, 0) + f(q, v, 1) = z h_\beta(v) \tag{11}$$

and we assume that the joint correlation functions satisfy (9) and condition (C):

$$\lim_{\varepsilon\to 0}\varepsilon^{2n}\rho_n^\varepsilon(x_1,\sigma_1,\cdots,x_n,\sigma_n)=\prod_{j=1}^{n}f(q_j,v_j,\sigma_j) \tag{12}$$

uniformly on compact sets of $\Gamma_n(\tau)$, for some $\tau\geqq 0$.

If these assumptions hold, then

$$\lim_{\varepsilon\to 0}\varepsilon^{2n}\rho_n^\varepsilon(x_1,\sigma_1,\cdots,x_n,\sigma_n,t)=\prod_{j=1}^{n}f(q_j,v_j,\sigma_j,t), \tag{13}$$

with

$$f(q,v,\sigma,t)=f(q,v,t)\sigma+(zh_\beta(v)-f(q,v,t))(1-\sigma),$$

uniformly on compact sets of $\Gamma_n(\tau+t)$, $t>0$. The convergence at time t is somewhat weaker than the assumed convergence at time $t=0$. This weakening suffices however (and better should) to exclude the velocity-reversed state. If in (13) all velocities are reversed, then the convergence takes place on the velocity-reversed set $R\Gamma_n(t+\tau)=\Gamma_n(-t-\tau)\neq\Gamma_n(t+\tau)$ and therefore the condition (C) is violated. The correlations thus behave singularly with respect to velocity reversal in the limit $\varepsilon\to 0$.

4. Self-Diffusion at Finite Density

For a system at finite density one can derive hydrodynamic equations such as the self-diffusion equation by taking a continuum limit which is known as the *hydrodynamic limit*. For self-diffusion the hydrodynamic limit consists of scaling the fugacity as

$$z_\varepsilon=\varepsilon^{-3}z \quad \text{as} \quad \varepsilon\to 0 \tag{14}$$

and the time as

$$t_\varepsilon=\varepsilon^{-2}t. \tag{15}$$

The thermodynamic properties of the system do not change, only every distance shrinks by a factor ε. If one picks a point q in Λ and a little ball of radius εR around it, then the average number of particles in the ball is approximately independent of ε and their distribution, blown up by a factor ε^{-1}, is given by the infinite-volume equilibrium measure with parameters (z,β) restricted to a ball of radius R.

The macroscopic equation governing the evolution of the color profile at finite density is the diffusion equation

$$\frac{\partial}{\partial t}\rho(q,t)=D(z,\beta)\frac{\partial^2}{\partial q^2}\rho(q,t), \tag{16}$$

where $\rho(q,t)$ is the color density at time t in physical space, $D(z,\beta)$ is the self-diffusion constant depending on z and β. It is given by the Einstein formula

$$D(z,\beta)=\tfrac{1}{6}\int_0^\infty dt\,\langle v(t)\cdot v(0)\rangle. \tag{17}$$

Here $v(t)$ is the velocity of a given test particle at time t starting with velocity $v(0)$ in the *infinitely extended* hard sphere fluid. The average is over the equilibrium measure with parameters (z,β). We assume that this choice of parameters puts the system in the fluid phase. Otherwise a different macroscopic description might be necessary.

If one follows the pattern laid out in the previous section, one is led to

CONJECTURE 2. *Using the scaling* (14),

$$\lim_{\varepsilon\to 0}\varepsilon^{3}N_1^\varepsilon(\varepsilon^{-2}t)=\int_{\Lambda_1}dq\,\rho(q,t) \tag{18}$$

in probability, where $\rho(q,t)$ is the solution of the diffusion equation with initial data $\rho(q)=\chi_{\Lambda_1}(q)$.

This again has the interpretation that for a given error bar $\delta>0$ one can choose ε small enough such that, with the exception of dynamical states of total weight less than δ, the color profile of every dynamical state follows the diffusion equation within an error δ. Again "good" initial configurations are characterized only probabilistically. Given a particular configuration one has no way to tell whether its color profile follows the macroscopic equation or not.

One does not know how to prove (18) or even the existence of (17) except in very special model systems (cf. [13], [14]). In fact, Conjecture 2 is believed to be wrong in two dimensions since (17) is expected not to converge there (cf. [15]). We are able, however, to reformulate Conjecture 2 in a way which shows clearly the properties of the dynamics of interacting systems which are responsible for observed diffusive behavior. Unlike those for the low density regime, the technical problems are far from solved.

As explained before, the moments of $N_1^\varepsilon(t)$ can be computed from the knowledge of the transition probabilities of test particles. If one takes into account the boundary conditions by a separate argument, then one is led to the following problem: We consider an *infinitely extended* hard sphere fluid in thermal equilibrium and select a particle which will be considered as the test particle. We then follow the system, including the test particle, as it evolves in time. We denote the velocity of the test particle at time t by $v(t)$; $v(0)$ is distributed according to the Maxwellian $h_\beta(v)\,dv$. Since the equilibrium Gibbs distribution [illegible] of the fluid is stationary in time, $v(t)$ is a *stationary*

stochastic process. The displacement $q(t)$ of the test particle at time t is, of course,

$$q(t) = \int_0^t ds\, v(s). \tag{19}$$

The hydrodynamic limit for self-diffusion translates to the test particle process as

$$q^\varepsilon(t) = \varepsilon \int_0^{\varepsilon^{-2}t} ds\, v(s). \tag{20}$$

Conjecture 2 will then become a theorem if we can show that, (i)

$$\lim_{\varepsilon \to 0} q^\varepsilon(t) = b(D(z,\beta)t) \tag{21}$$

with $b(t)$ standard Brownian motion and (ii) two test particles become independent in this limit. In particular we want the transition probability for $q^\varepsilon(t)$ to converge as $\varepsilon \to 0$ to the transition probability of Brownian motion, i.e., to the fundamental solution of the diffusion equation (16).

Note that (21), if proved, would be nothing else than the *central limit theorem* for the stationary stochastic process $v(t)$. Central limit theorems are well known from other areas of statistical physics and has belonged to the core of probability theory for ever. Intuitively the central limit theorem for $v(t)$ should hold, because the velocities of the test particle at microscopically widely spaced time instants

$$v(0), v(\varepsilon^{-1}), v(2\varepsilon^{-1}), \cdots, v(\varepsilon^{-1}t\varepsilon^{-1})$$

should be approximately independent. The crucial point is here in what precise sense they are independent. It is certainly not sufficient that the autocorrelation function in (17) decays in an integrable way. Physically it seems reasonable to expect that $v(t)$ becomes independent of $v(0)$ for large t, because of the many collisions in between. These collisions lead to forgetting of the initial velocity. But this is precisely the difficult dynamical problem which has to be resolved.

5. The Lorentz Gas and the Theorem of Bunimovich and Sinai

In a simplified version of the self-diffusion problem Bunimovich and Sinai [11] prove the above-mentioned central limit theorem. Although their model is very idealized, we believe that their result is a very important step in understanding the connection between microscopic dynamics and macroscopic laws.

In this simplified model, known as the Lorentz gas (cf. [16]), one considers *independent* point particles which move in an external potential created by static scatterers. The scatterers are assumed to be spherical and particles are specularly reflected at their surface. Disregarding the color, which they still carry, either black or white, the fugacity (density) of the particles is z and their velocities are uniformly distributed over the surface of a sphere in velocity space with center at the origin and radius $|v|$. As before we assume that initially all particles in Λ_1

are black and those in Λ_2 are white. For the Lorentz gas one can restrict oneself immediately to the motion of a *single* particle among all the scatterers, but we shall not do this in order to keep the connection with the interacting model. In fact, if one imagines that the scatterers are transparent and that there are many of them with a diameter of microscopic size, then on the macroscopic scale the visual impression of the time evolution of the color profile will not be changed at all compared to the interacting model.

In the usual version of the Lorentz gas one assumes that the scatterers are distributed randomly, typically like the particles in an ideal gas with density ρ. For the low density regime the Boltzmann–Grad limit is then

$$\begin{aligned} &\text{diameter of a scatterer} = \varepsilon d, \\ &\text{density of scatterers} = \varepsilon^{-2}\rho, \\ &\text{fugacity of the particles} = \varepsilon^{-2}z, \\ &\varepsilon \to 0. \end{aligned} \tag{22}$$

With this scaling Proposition 1 holds. Only the linear Boltzmann equation has to be changed slightly, since at a collision the scatterer does not recoil:

At finite density the color profile will again be governed by the diffusion equation if we can prove (21). This has so far not been done for a random configuration of scatterers. (We offer a bottle of good champagne for its solution.) Bunimovich and Sinai consider instead the *periodic* Lorentz gas, i.e., they take a basic cubic cell of length l with spherical scatterers and repeat it periodically. The configuration of scatterers in the basic cell is quite arbitrary except for the assumption of a *finite horizon*, which means that there is no unbroken particle path all the way to infinity. The hydrodynamic limit consists in shrinking the basic cell (together with the scatterers) by a factor ε, i.e.,

$$\begin{aligned} &\text{length of basic cell} = \varepsilon l, \\ &\text{fugacity of the particles} = \varepsilon^{-3}z, \\ &\text{time} = \varepsilon^{-\nu}t, \\ &\varepsilon \to 0. \end{aligned} \tag{23}$$

Given the length εl of the basic cell let the number of black particles in Λ_1 at time t be denoted by $N_1^\varepsilon(t)$. In general, one has to allow for anisotropy and the macroscopic equation then reads

$$\frac{\partial}{\partial t}\rho(q,t) = \sum_{i,j=1}^{3} \frac{\partial}{\partial q_i} D_{ij} \frac{\partial}{\partial q_j}\rho(q,t), \tag{24}$$

with some strictly positive matrix $\mathbf{D}$. The initial condition is $\rho(q) = \bar{z}\chi_{\Lambda_1}(q)$ with $\bar{z}$ the effective density of black particles. As a consequence of the theorem by

Bunimovich and Sinai one has

PROPOSITION 3. *There exists a* $D>0$ *such that*

$$\lim_{\varepsilon\to 0}\varepsilon^3 N_1^\varepsilon(\varepsilon^{-2}t)=\int_{\Lambda_1} dq\,\rho(q,t) \tag{25}$$

in probability, where $\rho(q,t)$ *satisfies* (24).

(The theorem published in [13] refers to two dimensions, but extends to three.)

For the proof of (21) for this system it suffices to consider a single basic cell with periodic boundary conditions and a single particle moving among the scatterers – a model known as the Sinai billiard. We denote the velocity of the particle by $v(t)$. The initial position of the particle is distributed uniformly over the space outside the scatterers and its initial velocity uniformly over the surface of the sphere in velocity space with center at the origin and radius $|v|$. Then $v(t)$ is a stationary stochastic process. One would like to prove the central limit theorem for $v(t)$ in the sense that

$$q^\varepsilon(t)=\varepsilon\int_0^{\varepsilon^{-2}t} ds\,v(s) \tag{26}$$

tends in the limit $\varepsilon\to 0$ to three-dimensional Brownian motion with diffusion matrix **D**. This convergence to Brownian motion is the content of the theorem by Bunimovich and Sinai. To prove it, they make use of the good ergodic properties of the Sinai billiard which have their origin in the defocusing of velocities at collisions. If in the two-dimensional periodic Lorentz gas the circular scatterers are replaced by rectangular ones, then the system loses its good ergodic properties and presumably no central limit theorem for the velocity holds (cf. [17]). The color profile would then evolve non-diffusively.

6. Concluding Remarks

(i) The irreversible linear Boltzmann equation and the diffusion equation are consistent with the reversible Newtonian mechanics, since the approximation by the macroscopic equations is valid only for a particular class of statistically characterized initial configurations. The question of how to characterize "good" initial ensembles at finite density remains open. The low density case provides an illustration of what form such an answer might take, namely condition (C) at the end of Section 3. Condition (C) is time-asymmetric in just the right way – the property is preserved under the *forward* time evolution.

More precisely if (C) is satisfied on the set $\Gamma_n(\tau)$ for some positive τ (say one hour), then if the ensemble evolves for some positive t, (C) is still satisfied on the smaller set $\Gamma_n(\tau+t)$. If, however, we perform a velocity reversal at time

then (C) is no longer satisfied on any set $\Gamma_n(s)$, $s\geqq 0$. The same statements are true for τ, t both negative. The initial ensemble considered in our example is invariant under velocity reversal and therefore (C) is satisfied on $\Gamma_n(0)$, i.e., $\tau=0$. We can, therefore, derive either the forward or the backward (in time) linear Boltzmann equation (both leading to identical uniformization of the density as $|t|$ increases) *but* cannot go first in one direction and then "back-track" by using velocity reversal. It is this restriction which permits the derivation of irreversible equations from reversible dynamics and initial conditions which are symmetric under velocity reversal. Which way we actually go physically is determined by the fact that we are able to prepare the system, i.e., select the initial conditions of the experiment on "isolated" systems, not the final conditions.

(ii) Having considered self-diffusion at such length the reader may wonder about other transport processes in fluids and gases. First of all there is the question of what to expect and to conjecture. Here we claim that self-diffusion is *prototypical*. We just have to transcribe our results for self-diffusion to a somewhat more complicated situation encountered in real non-equilibrium fluids. To be brief we only sketch the outcome of this transcription.

The continuum limit appropriate for the low density regime is the Boltzmann–Grad limit. The macroscopic field of a dilute one-component gas is the number of particles, $n^\varepsilon(\Delta,t)$, in Δ at time t with Δ a Borel set in the one-particle phase space $\Lambda\times R^3$. In analogy to the self-diffusion problem we choose a continuous macroscopic distribution $f(q,v)\,dq\,dv$ and for every hard sphere diameter εd a "sufficiently regular" initial ensemble with the property that

$$\lim_{\varepsilon\to 0}\varepsilon^2 n^\varepsilon(\Delta,t=0)=\int_\Delta dq\,dv\,f(q,v) \tag{27}$$

in probability. That is, the discrete mass distribution, a sum of delta functions, $\varepsilon^2\sum\delta_{(q_j,v_j)}(dq\,dv)$ in the one-particle phase space approximates, almost surely, the continuous mass distribution $f(q,v)\,dq\,dv$. Note that the ε-dependence of the random variables $n^\varepsilon(\Delta,t)$ comes from the ε-dependence both of the initial ensemble and of the dynamics. We expect then that

$$\lim_{\varepsilon\to 0}\varepsilon^2 n^\varepsilon(\Delta,t)=\int_\Delta dq\,dv\,f(q,v,t) \tag{28}$$

in probability, where $f(q,v,t)$ is the solution of the nonlinear Boltzmann equation with initial data $f(q,v)$, i.e., the discrete mass distribution $\varepsilon^2\sum_j\delta_{(q_j(t),v_j(t))}(dq\,dv)$ at time t is well approximated by the solution $f(q,v,t)\,dq\,dv$ of the Boltzmann equation.

At finite density the appropriate limit is the hydrodynamic limit, which for hard spheres takes the form: hard sphere diameter εd, particle number density ε^{-3}, $\varepsilon\to 0$. The macroscopic fields are, at the least, the fields of all locally conserved quantities. For monatomic fluids one has five of them: the number,

$n_1^\varepsilon(\Delta, t)$, the center of mass velocity, $(n_2^\varepsilon(\Delta, t), n_3^\varepsilon(\Delta, t), n_4^\varepsilon(\Delta, t))$, and the energy, $n_5^\varepsilon(\Delta, t)$, of the particles in the *spatial* region $\Delta \subset \Lambda$ at time t. Again we choose a macroscopic mass density field $\rho(q) = n_1(q)$, velocity field $\rho(q)\vec{u}(q) = (n_2(q), n_3(q), n_4(q))$, and energy density field $\rho(q)e(q) = n_5(q)$ and for every hard sphere diameter εd a "sufficiently regular" ensemble with the property that

$$\lim_{\varepsilon \to 0} \varepsilon^3 n_j^\varepsilon(\Delta, t = 0) = \int_\Delta dq\, n_j(q), \qquad j = 1, \cdots, 5, \tag{29}$$

in probability. The full hydrodynamic equations of a compressible, viscous fluid have a reversible part, the Euler equations, which involves only thermodynamic coefficients and a dissipative part which contains the classical transport coefficients: bulk and shear viscosity and thermal conductivity. One expects then that

$$\lim_{\varepsilon \to 0} \varepsilon^3 n_j^\varepsilon(\Delta, t) = \int_\Delta dq\, n_j(q, t), \qquad j = 1, \cdots, 5, \tag{30}$$

in probability, where $n_j(q, t), j = 1, \cdots, 5$, are the solution of the *Euler* equations with initial data $n_j(q)$, $j = 1, \cdots, 5$. To see dissipation one has to follow the system over long times of the order $\varepsilon^{-2}t$ and one should insert in the right-hand side of (30) the solution of the full hydrodynamic equations including the Navier–Stokes correction. This situation should be compared with the one of a simple random walk with constant drift, where also *two time scales* enter: a fast one characterized by the reversible drift and a slow one characterized by the irreversible diffusion. For the hydrodynamic equations the problem of two time scales is not understood.

The conjectures (28) and (30) form a grand program. Fortunately some steps have been proved which makes us believe that we are at least heading the right way. Conjecture (28), at least for short times, is a consequence of Lanford's theorem. The restriction to short times is of a technical nature and very likely (28) is correct for all times. The technical difficulty appears, however, to be rather deep, which reflects the fact that up to now there is no satisfactory global existence theory for the solutions of the nonlinear Boltzmann equation.

The hydrodynamic limit on the level of the Euler equations has been proved by Boldrighini, Dobrushin, and Sukhov [18] for a one-dimensional system of hard rods. This system is rather degenerate, since instead of five it has infinitely many conservation laws: the number of particles with each given velocity is conserved. Therefore the Euler equations for hard rods have no resemblance to those of a real fluid. Still the example has its value, since it shows that our ideas of how to derive the hydrodynamic equations from the Newtonian dynamics of particles are not contradictory in themselves. All in all, however, we are still very far away from a real understanding of the connection between microscopic dynamics and macroscopic laws at finite density. This is the *big* question in non-equilibrium statistical mechanics at the present time (cf. [19]).

(iii) We sometimes wonder how our conception of the "arrow of time" would change if a method was found for actually reversing velocities in a fluid (or change appropriate quantum phases). We do not mean reverse all the velocities in the universe, but just in systems like that of our example. Just something modest which would permit the right side of Figure 1 to represent the result of an actual experiment in which the system was isolated beginning with t_1. Would this be just like the spin echo experiment (cf. [20]), which is now almost forgotten, or would this substantially change our concept of time's arrow? Put differently, do the laws of nature, as we understand them at present, exclude the possibility of ever observing the right side of Figure 1 in a real life experiment? The fact that trajectories are unstable may be relevant here: e.g. in the periodic Lorentz gas any approximate velocity reversal would have an effect that is very small on the hydrodynamic time scale. This suggests that good ergodic properties may be essential ingredients in understanding the irreversible macroscopic behavior. The absence of such good ergodic properties must lead, we believe, in some cases to effects which contradict our experience of irreversible behavior. Note however that the low density regime, or rather its zero density limit, is an exception: Lanford's theorem never uses the ergodic properties of hard spheres – it is equally valid for cubes with the appropriate modification of the collision kernel. The theorem, as it stands, relies entirely on the absence of recollisions in the limit.

(iv) To emphasize the importance of the macroscopic size of the system in the observation of irreversible behavior, note that the example in Figure 1 would not make much sense if there were only a few particles in the system. Systems with few degrees of freedom can certainly exhibit instabilities in their trajectories. They can even be Bernoulli as the baker's transformation or Sinai's billiard is. For small systems of these types, any reasonable initial ensemble will behave irreversibly but a single system *will not* exhibit irreversible behavior. For a macroscopic system, however, a single system can give observational results which we would call irreversible as in the above example. Put differently, there is no reasonable kinetic equation for describing the behavior of a system with a few degrees of freedom. The fluctuations about any ensemble average are just too large.

The unstable behavior of trajectories of nonlinear dynamical systems with a few degrees of freedom can thus only serve as one ingredient in the derivation of kinetic equations describing the time evolution of real macroscopic variables. This is so despite the fact that the study of the consequences of good ergodic properties on the behavior of measures absolutely continuous to a given stationary measure may be directly relevant to the behavior of ensembles for macroscopic systems.

The situation here is similar to, but much less well understood than the situation in equilibrium. While the use of equilibrium Gibbs ensembles is formally the same for systems of few or many particles, the relation between ensemble

averages and observations is quite different in the two cases. It is only for systems of macroscopic size that the ensemble average gives reliable predictions of observations on individual systems.

Appendix

Statistical Characterization of "Good" Phase Points

We emphasized repeatedly that initial dynamical states which are compatible with the kinetic equation are only statistically characterized. Although this is common understanding within statistical physics, a simple example, quite remote from the problems discussed in this article, might help elucidate this point further.

Let us consider the now fashionable dynamical system with discrete time given by a map f of the unit interval $[0, 1]$ into itself. We choose a starting point $x_0 \in [0, 1]$ and iterate through f as

$$x_1 = f(x_0), \cdots, x_{n+1} = f(x_n). \tag{1}$$

The sequence $x_0, x_1, \cdots$ is the trajectory (orbit) of our dynamical system. To be specific let us choose $f(x) = 2x$ for $0 \leqq x \leqq \frac{1}{2}$ and $f(x) = 2x - 1$ for $\frac{1}{2} < x \leqq 1$. Then the Lebesgue measure dx is invariant under f and one knows that for dx-almost all starting points

$$\lim_{n\to\infty} \frac{1}{n} \sum_{j=0}^{n-1} \delta_{x_j}(dx) = dx, \tag{2}$$

in the sense of weak convergence of probability measures. The histogram of a typical trajectory spreads out uniformly on $[0, 1]$ as $n \to \infty$. (If one wants to push the analogy with our main theme, one could call dx the "macroscopic" law.) Of course the histogram of a *given* starting point x_0 may look very different from dx. An example of such a "bad" point is $x = \frac{1}{3}$ whose histogram is concentrated with equal weight on $x = \frac{1}{3}$ and $x = \frac{2}{3}$. For our choice of f we have however a simple algorithm to decide on the histogram of an orbit with starting point x_0: in the binary expansion of x_0 the map f translates into the shift to the left and dx gives equal weight to every sequence of 0, 1 symbols (Bernoulli measure).

If we complicate the situation only slightly by choosing as our dynamical system the map $f(x) = \sin \pi x$, then we are still assured (cf. [21]) of the existence of a unique invariant measure $h(x)\,dx$ which is absolutely continuous with respect to the Lebesgue measure. We are also assured that for dx-almost all starting points

$$\lim_{n\to\infty} \frac{1}{n} \sum_{j=0}^{n-1} \delta_{x_j}(dx) = h(x)\,dx$$

weakly. We no longer have, however, a simple algorithm which tells us whether the histogram of the orbit of a particular starting point x_0 approximates $h(x)\,dx$

within a certain precision. We have to be satisfied with a statistical characterization of "good" starting points. Such an algorithm is not forbidden. We might try to construct one by finding a conjugacy between $\sin \pi x$ and $1 - 2|x - \frac{1}{2}|$. The point is, however, that in general a statistical characterization is the simpler thing to achieve.

If we numerically iterate the map $x \to \sin \pi x$, we will *always* find the same histogram no matter what the starting point, provided we "just" pick x_0 and avoid the obviously bad points $x = 0, \frac{1}{2}, 1$. This may be tested on any computer nearby. Since, however, the machine is built with a *finite* number of internal states and proceeds from one well-defined internal state to the next one in a deterministic fashion, it always produces a periodic orbit with a possibly rather long period. In a first step to understand why the histogram of this periodic orbit approximates so well the invariant distribution, provided the resolution is not too high, one would have to scrutinize the way the machine works, its procedure to compute the sine, round off conventions, etc. Somehow there may be a vague analogy between the numerical realization of a map on the unit interval and our limited macroscopic control over microscopic systems with many particles.

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