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Microscopic Basis for Fick's Law for Self-Diffusion[1]

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We investigate self-diffusion in a classical fluid composed of two species which are distinguished through the color of their particles, either black or white, but are identical as regards their mechanical properties. Disregarding color the fluid is in thermal equilibrium. We show that if a single "test particle" in the one-component fluid moves asymptotically as Brownian motion, then the color density and current in certain classes of nonequilibrium states are related, on the appropriate macroscopic scale, through Fick's law, and the former is governed by the diffusion equation. If in addition several test particles move asymptotically as independent Brownian motions, then the colored fluid is, on a macroscopic scale, in local equilibrium with parameters governed by the solution of the diffusion equation.

KEY WORDS: Diffusive motion; test particles; classical fluid; convergence to Brownian motion; steady state self-diffusion; Fick's law.

1. INTRODUCTION

The mathematical formalism of statistical mechanics, relating macroscopic behavior to microscopic dynamics, is not entirely satisfactory for systems out of equilibrium. This is true even close to equilibrium, when the behavior of the macroscopic variables is governed by well-established hydrodynamic equations. One of the conceptual problems encountered is that of defining in a precise way the continuum variables which enter into the macroscopic transport laws. Consider, for example, Fourier's law of

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heat conduction,

$$j(q,t) = -\kappa(\rho, T)\text{grad}\, T(q,t) \tag{1.1}$$

where $j(q,t)$ is the energy flux at position q and time t, $T(q,t)$ is the "local temperature" at the same position and time, and κ is the thermal conductivity which is supposed to depend *only* on the local density and temperature. It is clear, since the gradient enters the law explicitly, that there is no way in which we can go to a scaleless thermodynamic limit as we do in equilibrium. What is not clear at all *a priori*, when starting with a microscopic model, is just on what scale (1.1) is supposed to be valid.

This problem appears also in the derivation of the Einstein–Green–Kubo formulas for the transport coefficients. Indeed while we believe that these are valid in many (perhaps all) cases we do not feel that any of the derivations available at present are entirely satisfactory. In particular none of the derivations seems applicable to the computation of transport properties in steady state experiments where the fluxes are driven by external, time-independent, (infinite) thermal reservoirs coupled to the system. We thus cannot show, even on a formal level, that the transport coefficients in the steady state equal those computed microscopically from the relaxation of local deviations from equilibrium.[1,2]

The main purpose of this paper and of two subsequent papers[3,4] is to investigate self-diffusion in a classical fluid of particles: conceptually and mathematically the simplest nonequilibrium phenomenon. We shall give sufficient criteria for the validity of the diffusion equation and the equality of the self-diffusion constant in time-dependent and steady state situations. It will turn out that the latter imposes stronger, albeit physically very reasonable, requirements on the large spatial and time scale motion of a test particle in an equilibrium fluid: not only need the probability distribution of the displacements at any one time be asymptotically Gaussian, they also have to be (on the appropriate scale) independent.

We shall not discuss in this paper the question of whether a system of particles interacting via some specified reasonable pair potential, e.g., Lennard–Jones or hard core, actually satisfies these hypothesis at any given density and temperature. This is an extremely difficult mathematical problem whose solution is nowhere in sight. The best we can do at present is to treat some very idealized systems. Two such cases, the low-density gas (Boltzmann–Grad limit) and the one-dimensional system of hard rods, are investigated in subsequent papers.[3,4]

The outline of the paper is as follows. In Section 2 we explain the problem somewhat more precisely and in Section 3 we define the microscopic model. In Sections 4 and 6 we discuss time-dependent and steady state color density and in Section 5 the relationship between current and

density gradient (Fick's law) is investigated. Finally, in Section 7 we discuss fluctuations and the local equilibrium structure and we draw some conclusions at the end.

2. FORMULATION OF THE PROBLEM

Self-diffusion, being inherently quasiequilibrium and linear, is one of the simplest transport phenomenon. Microscopically it is measurable through the incoherent part of the neutron scattering cross section[5] and can also be studied readily in computer simulations.[6,7] Macroscopically it is best approached, in principle at least, by considering a binary mixture of fluids which are mechanically identical but differ according to some quality, say, color. (All our considerations are classical; in quantum mechanics the problem is more complicated.) We can then consider situations in which for a fluid in equilibrium at density ρ, the color density $\rho n(q,t)$ is a hydrodynamic variable which varies on a macroscopic spatial and time scale. The object of our study is the microscopic basis of the laws governing the behavior of $n(q,t)$ under various (realizable or imaginary) experimental conditions.

Let us consider two such situations:

(1) We start at time $t = 0$ with an equilibrium system in which there is some non-uniform color density $\rho n(q,0)$. For example, the color is all black to the left of a plane passing through the origin perpendicular to the x axis and all white to the right of that plane. We shall write this as

$$n(q,0) = \begin{cases} 1, & q_x < 0 \\ 0, & q_x > 0 \end{cases} \tag{2.1}$$

The phenomenological law governing the evolution of n is

$$\frac{\partial}{\partial t} n(q,t) = D \frac{\partial^2}{\partial q^2} n(q,t) \tag{2.2}$$

where the self-diffusion constant D depends only on the equilibrium density and temperature and is thus independent of q and t.

(2) In an (infinite) equilibrium system we single out a slab of width L perpendicular to the x axis for the sole purpose of imposing boundary conditions on the colors. All particles to the left of the slab are black and all particles to the right of the slab are white. If a particle inside the slab exits to the left, then its color is changed to (or remains) black and if it exits to the right, then its color is changed to (or remains) white. Aside from this change of colors the system is in equilibrium.[6,7] These boundary conditions ensure that a constant current of black particles enters the slab from the left and that a constant current of white particles enters the slab from

the right. Under these boundary conditions a steady state should be reached in which the color profile $\rho n_s(q)$ and current $j_s(q)$ have the form

$$n_s(q) = \begin{cases} 1 & q_x < 0 \\ (L - q_x)/L, & 0 \leqslant q_x \leqslant L \\ 0 & q_x > L \end{cases} \tag{2.3}$$

$$j_s(q) = \begin{cases} D_s \rho e_x / L, & 0 \leqslant q_x \leqslant L \\ 0, & q_x < 0, q_x > L \end{cases} \tag{2.4}$$

e_x is the unit vector pointing in the positive x direction.

The problem then is to give a microscopic derivation, under suitable assumptions, of Eqs. (2.2)–(2.4) and *ipso facto* to show that $D_s = D$. Now from the macroscopic point of view, the behavior in both cases is a consequence of Fick's law for the current,

$$j(q,t) = -D \operatorname{grad} \rho n(q,t) \tag{2.5}$$

When (2.5) is combined with the equation of continuity for the color density,

$$\frac{\partial}{\partial t} \rho n(q,t) + \operatorname{div} j(q,t) = 0 \tag{2.6}$$

we obtain (2.2). The relation (2.5) being "local" it also implies that $n_s(q)$ is given by the stationary solution of (2.2) with appropriate boundary conditions. The central problem is therefore the derivation of (2.5) as a relation between microscopically defined independent quantities when these are appropriately scaled. The continuity equation follows from microscopic color conservation.

The simplest microscopic interpretation of $\rho n(q,t)$ is as the average single-particle density, $\rho_1(q,t)$, of black particles in an ensemble which is in equilibrium with respect to the uncolored particles, i.e., when looked at with "color blind" glasses. Clearly, however, if no further restrictions are imposed on the state at the initial time, then there is no hope that $\rho_1(q,t)$ will, even approximately, be governed by the diffusion equation (2.2) for any fixed finite time t. (Examples of "bad" initial states can be obtained through velocity reversal.) Physically one expects that if initially color and mechanical degrees of freedom are "sufficiently uncorrelated," then $\rho_1(q,t)$ satisfies (2.2), at least approximately. We shall therefore consider situations in which the microscopic state corresponding to the color density (2.1) (and similar cases) corresponds to the color distribution of a particle depending *only* on its location. We then have[5]

$$\rho_1(q,t) = \int dq' \, P_s(q,t \mid q',0) \rho_1(q',0) \tag{2.7}$$

where $P_s(q,t \mid q',0)$ is the van Hove self-function which gives the probability density for finding a specified particle (test particle) at position q at time

t given that it was at position q' and had Maxwellian velocity distribution at time zero, $P_s(q,0\,|\,q',0) = \delta(q-q')$. Since the system is in equilibrium, $P_s(q,t\,|\,q',0) = P_s(q,t+s\,|\,q',s)$, and if the system is also translation invariant, then $P_s(q,t\,|\,q',0) = P_s(q-q',t\,|\,0,0)$. A little thought shows that even here it is only for large q and t, related by the scale invariance of the diffusion equation, i.e., time $\sim\epsilon^{-2}$ and space $\sim\epsilon^{-1}$, $\epsilon \ll 1$, where one can expect (or hope) that $P_s(q,t\,|\,0,0)$ will behave like the solution of the diffusion equation and thus we should identify $n(q,t)$ of (2.2) as

$$\rho n(q,t) = \lim_{\epsilon\to 0} \rho_1(\epsilon^{-1}q, \epsilon^{-2}t) \tag{2.8}$$

Also in the steady state experiment (2) the density and current of (2.3) and (2.4) should be identified as

$$\rho n_s(q) = \lim_{\epsilon\to 0} \rho_1(\epsilon^{-1}q; \epsilon^{-1}L) \tag{2.9}$$

$$j_s(q) = \lim_{\epsilon\to 0} \epsilon^{-1} j(\epsilon^{-1}q; \epsilon^{-1}L) \tag{2.10}$$

where $\rho_1(q;L)$ is the microscopic steady state average density and $j(q;L)$ the microscopic steady state average current of black particles at q for a slab of width L.

Our first task is then to investigate the conditions on the systems which ensure that (2.5) holds for the scaled average color density in situations of the type considered here. We would like to do more, however. In analogy with equilibrium one expects physically that not only averages but also typical configurations of macroscopic systems will obey the macroscopic laws. Therefore eventually one should derive the following more refined description: At time t in a macroscopically small region around the point q such that the color density $\rho n(q,t)$ can be considered as almost constant, the fraction $n(q,t)$ of particles is black and the fraction $1-n(q,t)$ of particles is white. If this is the case, then the *actual* density of black particles is governed by the diffusion equation. In addition, the fluid, considered on a macroscopic scale, is locally in thermodynamic equilibrium. The parameters determining this local equilibrium state are color density, particle density, and temperature. The latter two are fixed while the former changes on a macroscopic scale and its local value is governed by the solution of the diffusion equation (2.2).

3. MICROSCOPIC MODEL

We consider an infinitely extended system of classical particles carrying color. The phase space of the system Ω, is the space of configurations, i.e., the space of sequences $\{q_j, p_j, \sigma_j \,|\, j \in N\}$ modulo permutations such that $q_j \in R^3$, $p_j \in R^3$, $\sigma_j \in \{0,1\}$. q_j refers to the position, p_j to the velocity,

and σ_j to the color of the jth particle. $\sigma_j = 0$ corresponds to white and $\sigma_j = 1$ corresponds to black. Let Ω_p be the space of uncolored particle configurations, i.e., the space of sequences $\{q_j, p_j \mid j \in N\}$ modulo permutations. We will use the shorthand $x_j = (q_j, p_j)$ and $x = \{x_j \mid j \in N\}$.

The particles interact through a central pair potential which we assume to satisfy conditions ensuring that the equilibrium dynamics exists in the thermodynamic limit and is unique.[8-10] As long as no color-changing conditions are imposed color simply sticks to a particle. The particles are in thermal equilibrium at density ρ and inverse temperature β. We assume that the system exists in a single phase with decaying correlations. Let μ be the unique equilibrium state on Ω_p at these parameters. ρ_{eq} denotes the vector of correlation functions of μ and h_β the Maxwellian at inverse temperature β.

We consider now the motion of one or several test particles in the colorless system of particles. These test particles are mechanically identical to all other particles. Let us describe first the motion of a single test particle. The phase space of the joint system, test particle plus fluid particles, is

$$\Omega_1 = R^6 \times \Omega_p$$

R^6 is the phase space of the test particle. Let $\mu(\cdot \mid q, p)$ be the Gibbs state conditioned that there is a particle at q with velocity p. Then the (unnormalized) measure

$$\mu_1 = \mu(dx \mid q, p)\, dq\, h_\beta(p)\, dp \tag{3.1}$$

on Ω_1 is formally time invariant. Exploiting this fact one can use the same argument which proves the existence of equilibrium dynamics to establish that for μ_1—almost all initial conditions the dynamics

$$T_t : \{q, p, x\} \to \{q(t), p(t), x(t)\} \tag{3.2}$$

exists and is unique. $\{q(t), p(t), x(t)\}$ are the solution of Newton's equation of motion with initial conditions (q, p, x). The equilibrium probability distribution in the system's coordinates and velocities induces a probability distribution on the trajectories of the test particle, e.g., the position $q(t)$ of the test particle at time t is a random variable on $\{R^6 \times \Omega_p, \mu_1\}$. Since $t \to q(t)$ is continuous, $q(t)$ is a stochastic process with continuous sample paths. Let $C(R)$ be the space of continuous functions on R with values in R^3. $C(R)$ restricted to bounded intervals is equipped with the sup-norm, as usual. Then $x \to q(t, q, p, x)$ induces $dq\, dp$—almost surely a probability measure on $C(R)$, the path measure of the stochastic process $q(t)$ starting at q with velocity p. By a similar argument, one establishes the existence of the stochastic process of the motion of n test particles.

We use the following notation: $q_1(t), \ldots, q_n(t)$ are the positions of n test particles at time t considered as a stochastic process. $t \to \{q_1(t), \ldots, q_n(t)\}$ is continuous and $P(\cdot \mid q_1, p_1, \ldots, q_n, p_n)$ denotes the path measure on $C(R, R^{3n})$ for this process conditioned the test particles start at $q_1, \ldots, q_n$ with velocities $p_1, \ldots, p_n$. $E(\cdot \mid q_1, p_1, \ldots, q_n, p_n)$ denotes expectation with respect to this measure.

4. TIME-DEPENDENT STATES

It follows from the general results of equilibrium statistical mechanics that if one starts the test particle at $q(0)$ with a Maxwellian velocity distribution, then the velocity process $\{p(t) \mid -\infty < t < \infty\}$ is stationary and has mean zero. Because of collisions one expects that the velocities $p(t)$ at widely spaced time intervals are weakly correlated and that therefore

$$q(t) = q(0) + \int_0^t ds\, p(s) \tag{4.1}$$

satisfies a central limit theorem when scaled in an appropriate way, i.e., the distribution $w_{t,\epsilon}(dq)$ of the random variable

$$q^\epsilon(t) = \epsilon q(0) + \epsilon \int_0^{\epsilon^{-2}t} ds\, p(s) \equiv \epsilon q(\epsilon^{-2}t) \tag{4.2}$$

containing t as a parameter should tend to a Gaussian as $\epsilon \to 0$. We shall call this Assumption A:

$$w_{t,\epsilon}(dq) \to (4\pi D_0 t)^{-3/2} \exp\left[-(q - q_0)^2/2D_0 t\right] dq \tag{4.3}$$

Assumption A is sufficient to deal with initial states where the color of a particle depends only on its position. Let $g(q)$, $0 \leqslant g(q) \leqslant 1$, be a continuous function of q and let

$$\begin{aligned} g(q, 1) &= g(q) \\ g(q, 0) &= 1 - g(q) \end{aligned} \tag{4.4}$$

Given a configuration of particles, we assume that the particle at q_j has color σ_j with probability $g(q_j, \sigma_j)$ independently of all the other particles. g is then the profile of the black particles. The correlation functions of this initial state are given by

$$\rho_n(x_1, \sigma_1, \ldots, x_n, \sigma_n, 0;\, g) = \rho_{\text{eq}}(x_1, \ldots, x_n) \prod_{j=1}^{n} g(q_j, \sigma_j) \tag{4.5}$$

The correlation functions of the time evolved state at time t are denoted by

$$\rho_n(x_1, \sigma_1, \ldots, x_n, \sigma_n, t;\, g)$$

We consider a slowly varying color profile by setting

$$g^{\epsilon}(q) = g(\epsilon q) \tag{4.6}$$

$\epsilon \ll 1$, and follow the evolution of colors over times of the order ϵ^{-2} by means of the scaled correlation functions

$$\rho_n^{\epsilon}(x_1, \sigma_1, \ldots, x_n, \sigma_n, t;\, g) = \rho_n\left(\epsilon^{-1}q_1, p_1, \sigma_1, \ldots, \epsilon^{-1}q_n, p_n, \sigma_n, \epsilon^{-2}t;\, g^{\epsilon}\right) \tag{4.7}$$

The average number of black particles in the volume Δ at time t equals the average number of particles in Δ times the probability that the particle at q in Δ at time t is black, which is the same as the probability that it was black at time zero. It follows then that the nth correlation function is given by the motion of n test particles as

$$\rho_n^{\epsilon}(x_1, \sigma_1, \ldots, x_n, \sigma_n, t;\, g) = \rho_{\mathrm{eq},n}\left(\epsilon^{-1}q_1, p_1, \ldots, \epsilon^{-1}q_n, p_n\right) \times E^{\epsilon}\left(\prod_{j=1}^{n} g\left(q_j^{\epsilon}(t), \sigma_j\right) \mid q_1, -p_1, \ldots, q_n, -p_n\right) \tag{4.8}$$

To obtain (4.8) we used the time invariance and time-reversal invariance of the equilibrium measure.

By Assumption A the average color profile tends to

$$\lim_{\epsilon \to 0} \rho_1^{\epsilon}(x_1, \sigma_1, t;\, g) = h_{\beta}(p_1)\rho g(q_1, \sigma_1, t) \tag{4.9}$$

where $g(q, \sigma, t) = \sigma g(q, t) + (1 - \sigma)(1 - g(q, t))$ and where $g(q, t)$ is the solution of the diffusion equation (2.2) with initial conditions $g(q, 0) = g(q)$ and diffusion constant D_0.

Generally, D_0 is identified with the diffusion coefficient D defined by the asymptotic mean square displacement

$$D \equiv \lim_{t \to \infty} \frac{1}{6t} \int dp\, h_{\beta}(p) E\left(q^2(t) \mid 0, p\right) \tag{4.10}$$

If the velocity autocorrelation function is absolutely integrable, then D can be computed as the time integral over the velocity autocorrelation function (Einstein relation),

$$\begin{aligned} D &= \lim_{t \to \infty} 1/6t \int_0^t ds \int_0^t ds' \int dp\, h_{\beta}(p) E\left(p(s) \cdot p(s') \mid 0, p\right) \\ &= \int_{-\infty}^{\infty} dt \int dp\, h_{\beta}(p) E\left(p(t) \cdot p(0) \mid 0, p\right) \end{aligned} \tag{4.11}$$

where we used the stationarity of the velocity process. Note, however, that (4.3) and (4.10) do not imply each other in general. The identification of D_0

with D requires that the second moment of $q^\epsilon(t)$ converges as $\epsilon \to 0$ to the second moment of the limit (4.3). [In two dimensions (4.3) and (4.11) may of course not exist at all; cf. Ref. 5.]

5. FICK'S LAW

To obtain Fick's law or even the macroscopic steady state profile and current in example (2) of Section 2, (4.3) turns out to be too weak an assumption. To strengthen it we note that if the system behaves as expected on physical grounds, i.e., in three dimensions has a strong decay of velocity correlations, then also the joint distribution of

$$[q^\epsilon(t_1) - q^\epsilon(0), q^\epsilon(t_2) - q^\epsilon(t_1)]$$

should be independent and Gaussian as $\epsilon \to 0$, and similarly for any finite collection of such terms. Let $b(t)$ be Brownian motion in three dimensions with covariance $2Dt$. Then the convergence just described means that the finite-dimensional distributions of $q^\epsilon(t)$ converge to those of $q + b(t)$. To be able to analyze our steady state experiment we will need to control the probability of events which depend on a continuum of times and not just on a finite number of them. (An event of this type is for example $\{t \to q(t) \,|\, |q(t)| \leqslant R \text{ for } 0 \leqslant t \leqslant 1\}$. Whether up to time one the test particle stays inside a ball of radius R cannot be decided on the basis of finitely many observations.) For convenience we adopt a convergence notion familiar from probability theory.

Assumption B. Let $b(t)$ be Brownian motion in three dimensions with covariance $2Dt$. Then, with $q(0) = \epsilon^{-1}q$,

$$q^\epsilon(t) \to q + b(t) \tag{5.1}$$

as $\epsilon \to 0$, in the sense of weak convergence of the path measures $P^\epsilon(\cdot \mid q, p)$ on $C(R)$.

We now show that as a consequence of Assumption B the macroscopic current is related to the macroscopic density by Fick's law (2.5).

Let S be a planar surface of finite area with a smooth boundary. Let $\mathbf{n}$ be a unit vector perpendicular to S. We denote by $j(S, [t_1, t_2])$ the average, in the initial state defined by (4.5), number of black particles crossing the surface S in the direction $\mathbf{n}$ during the time interval $[t_1, t_2]$ minus the average number of black particles crossing the surface S in the direction $-\mathbf{n}$ during the same time interval. This is the integrated current of black particles through S from t_1 to t_2.

For mechanical motion the above definition makes sense. For Brownian motion, however, the path wiggles a lot and the given definition of the integrated current is meaningless. One has to incorporate directly the

cancellations which occur when the path wiggles along S. One way to do this is to introduce a surface S' such that $S \cup S'$ is a plane. A crossing through S in $[t_1, t_2]$ is counted (with the proper sign) if either there is only one such crossing in the interval or the crossings are separated by at least one crossing through S'. With this convention we define on the path space $C(R)$ the function $F(S,[t_1,t_2])$ which assigns to the path $t \to q(t)$ the number of its crossings through S during the time interval $[t_1, t_2]$. $F(S,[t_1, t_2])$ takes integer values. It is defined almost surely with respect to the test particle process and with respect to Brownian motion.

For a given configuration of colored particles one counts how often each one of the black particles crosses S during $[t_1, t_2]$. If the particle for which the crossings are counted is regarded as the test particle, then one obtains the identity

$$j(S,[t_1,t_2]) = \int dx_1 \rho_{\mathrm{eq},1}(x_1) E\big(F(S,[t_1,t_2]) \mid x_1\big) \tag{5.2}$$

For short times

$$\begin{aligned} \lim_{\delta \to 0} (1/\delta) j(S,[t,t+\delta]) &= \int_S d\bar{q}_1 \int dp_1 \mathbf{n} \cdot p_1 \rho_1(q_1, p_1, 1, t; g) \\ &\equiv \int_S d\bar{q}_1 \mathbf{n} \cdot j(q_1, t) \end{aligned} \tag{5.3}$$

where $d\bar{q}_1$ denotes the surface measure on S. Therefore

$$j(S,[t_1,t_2]) = \int_{t_1}^{t_2} dt \int_S d\bar{q}_1 \mathbf{n} \cdot j(q_1, t) \tag{5.4}$$

On a macroscopic scale we obtain then

$$\begin{aligned} \epsilon^3 j\big(\epsilon^{-1} S, [\epsilon^{-2} t_1, \epsilon^{-2} t_2]\big) &= \int_{t_1}^{t_2} dt \int_S d\bar{q}_1 \mathbf{n} \cdot \epsilon^{-1} j\big(\epsilon^{-1} q_1, \epsilon^{-2} t\big) \\ &\equiv \int_{t_1}^{t_2} dt \int_S d\bar{q}_1 \mathbf{n} \cdot \epsilon^{-1} j^{\epsilon}(q_1, t) \\ &= \int dx_1 \rho_{\mathrm{eq},1}(x_1) E^{\epsilon}\big(F(S,[t_1,t_2]) \mid x_1\big) \end{aligned} \tag{5.5}$$

Note that $F(S,[t_1,t_2])$ is independent of ϵ. By Assumption B $q^{\epsilon}(t) \to q_1 + b(t)$ as $\epsilon \to 0$. If this convergence holds also for the expectation of the unbounded function $F(S,[t_1,t_2])$, then the right-hand side of (5.5) converges to

$$\int dq\, \rho g(q) E^{\circ}\big(F(S,[t_1,t_2]) \mid q\big) = -D \int_{t_1}^{t_2} dt \int_S d\bar{q}\, \mathbf{n} \cdot \operatorname{grad} \rho g(q,t) \tag{5.6}$$

Here E° denotes expectation with respect to Brownian motion. Comparing with (5.5) we conclude that

$$\lim_{\epsilon \to 0} \epsilon^{-1} j^{\epsilon}(q,t) = -D \operatorname{grad} \rho g(q,t) \equiv j(q,t) \tag{5.7}$$

The convergence here is in the sense of (5.5), namely, (5.7) holds when integrated over arbitrary time intervals $[t_1, t_2]$ and planar surfaces S. (5.7) shows that the properly scaled microscopic current of black particles tends in hydrodynamic limit to $(-D)$ times the gradient of their macroscopic density.

6. STEADY STATE

We first show that imposing boundary conditions on the colors at the planes through $q_x = 0$ and $q_x = L$ as in (2) of Section 2 leads to a steady state. We assume that initially all particles inside the slab, denoted by Λ, are black and argue that for $t \to \infty$ the system of colored particles reaches a steady state. This is proved by a monotonicity argument. Let us introduce the following events for the test particle process $q(t)$:

$$A(0,t) = \text{set of all continuous paths which within } [0,t] \text{ exit } \Lambda \text{ first to the right;}$$

$$A(1,t) = \text{set of all continuous paths which within } [0,t] \text{ either exit } \Lambda \text{ first to the left or stay inside } \Lambda;$$

$$A(\sigma, \infty) \equiv A(\sigma).$$

We adopt the convention that if the path starts already outside Λ, then this is considered as an exit. Let $\rho_n(x_1, \sigma_1, \ldots, x_n, \sigma_n, t; L)$ be the nth correlation function of the state of the system at time t. Then the average density of white particles at (q, p) at time t equals the average density of particles at (q, p) times the probability that given there is a particle at (q, p) at time t it is white. This is just the probability that going backwards in time for a time span t the test particle has exited Λ first to the right. Therefore, in general,

$$\rho_n(x_1, \sigma_1, \ldots, x_n, \sigma_n, t; L) = \rho_{\text{eq},n}(x_1, \ldots, x_n) \times P\left[\bigtimes_{j=1}^{n} A(\sigma_j, t) \,|\, q_1, -p_1, \ldots, q_n, -p_n \right] \quad (6.1)$$

$A(0,t)$ increases to $A(0)$ and $A(1,t)$ decreases to $A(1)$ as $t \to \infty$. Therefore $\rho_1(x_1, 0, t; L)$ increases and $\rho_1(x_1, 1, t; L)$ decreases to its limit as $t \to \infty$. For higher correlation functions one notices that they are expressible as linear combinations of the probability of product of events depending on a single color only. For example,

$$\rho_2(x_1, q, x_2, 0, t; L) = \rho_{\text{eq},2}(x_1, x_2) \times \{ -P(A(1,t) \times A(1,t) \,|\, q_1, -p_1, q_2, -p_2) + P(A(1,t) \times C(R) \,|\, q_1, -p_1, q_2, -p_2) \} \quad (6.2)$$

The events depending only on white increase and the events depending only on black decrease to their limit. Therefore every correlation function is a sum of either increasing or decreasing terms. As $t \to \infty$ the correlation functions then tend to the stationary limit

$$\rho_n(x_1, \sigma_1, \ldots, x_n, \sigma_n; L) = \rho_{\mathrm{eq},n}(x_1, \ldots, x_n) \times P\Big(\bigtimes_{j=1}^{n} A(\sigma_j) \,|\, q_1, -p_1, \ldots, q_n, -p_n \Big) \quad (6.3)$$

These are the correlation functions of the steady state.

Presumably, although there is no proof to our knowledge, the event that test particles never exit Λ has probability zero. If this is the case, as is true if test particles are assumed to diffuse, then the steady state (6.3) is unique among those states which when summed over colors reduce to the equilibrium state.

The steady state correlation functions will be rather complicated. They contain, roughly on distances of the order of a mean free path, boundary layers and correlation between colors. A simplified description emerges on a macroscopic scale, i.e., on a spatial scale which is large compared to the mean free path. Therefore we let $L \to \infty$ as $L_\epsilon = \epsilon^{-1} L$ and consider the scaled correlation functions

$$\begin{aligned} \rho_n^\epsilon(x_1, \sigma_1, \ldots, x_n, \sigma_n; L) &= \rho_n\big(\epsilon^{-1} q_1, p_1, \sigma_1, \ldots, \epsilon^{-1} q_n, p_n, \sigma_n; \epsilon^{-1} L\big) \\ &= \rho_{\mathrm{eq},n}\big(\epsilon^{-1} q_1, p_1, \ldots, \epsilon^{-1} q_n, p_n\big) \\ &\quad \times P^\epsilon\Big(\bigtimes_{j=1}^{n} A(\sigma_j) \,|\, q_1, -p_1, \ldots, q_n, -p_n \Big) \end{aligned} \quad (6.4)$$

Notice that the event $\bigtimes_{j=1}^{n} A(\sigma_j)$ for the scaled test particle process does not depend on ϵ.

By Assumption B

$$\lim_{\epsilon \to 0} P\big(A(\sigma) \,|\, q_1, -p\big) = P^\circ\big(q + b(t) \in A(\sigma)\big) \quad (6.5)$$

the exit probability for Brownian motion. This is known explicitly and we therefore have

$$\lim_{\epsilon \to 0} \lim_{t \to \infty} P_1^\epsilon(q, p, \sigma, t; L) = \rho h_\beta(p)\, g_s(q, \sigma) \quad (6.6)$$

where $g_s(q, \sigma) = \sigma n_s(q) + (1 - \sigma)[1 - n_s(q)]$ and $n_s(q)$ is given (2.3).

The average steady state current of black particles is given by Fick's law, Eq. (5.7), replacing $j(q,t)$ and $g(q,t)$ there by $j_s(q)$ and $n_s(q)$. [To show this actually requires a small modification in the argument leading to (5.7) since the test particle now carries a color, $\sigma(t)$, which changes whenever the test particle crosses the surface of Λ according to the rules given above.] By

symmetry $j_s(q, L) = (j(L), 0, 0)$ and the scaled x component satisfies

$$\lim_{\epsilon \to 0} \epsilon^{-1} j(\epsilon^{-1} L) = \frac{D}{L} \rho \tag{6.7}$$

In particular, $D_s = D$ satisfying the Einstein–Green–Kubo relation (4.11).

The particular geometry of our steady state experiment was chosen for simplicity. One could imagine regions of more complicated shape and stochastic boundary conditions for the colors. The result will always be the same. On a macroscopic scale the steady state is given by the stationary solution of the diffusion equation with the appropriate boundary conditions. The steady state current is related to the steady state density by Fick's law.

7. FLUCTUATIONS AND LOCAL EQUILIBRIUM

Thus far we discussed the average color profile on a macroscopic scale. As a more detailed description we consider now the color *random* field.

Let $n^\epsilon(\Delta, \sigma, t)$ be the number of particles of color σ in the spatial region $\epsilon^{-1}\Delta = \{q \in R^3 \mid \epsilon q \in \Delta\}$ at time $\epsilon^{-2}t$. $n^\epsilon(\Delta, \sigma, t)$ is a random variable. From Assumption B we conclude that for its average

$$\lim_{\epsilon \to 0} \langle \epsilon^3 n^\epsilon(\Delta, \sigma, t) \rangle = \int_\Delta dq\, \rho g(q, \sigma, t) \tag{7.1}$$

in the time-dependent state with initial conditions given by (4.5) and

$$\lim_{\epsilon \to 0} \langle \epsilon^3 n^\epsilon(\Delta, \sigma, t) \rangle = \int_\Delta dq\, \rho g_s(q, \sigma) \tag{7.2}$$

in the steady state given by (6.3).

To obtain information on the variance and higher-order correlations we have to go even beyond Assumption B and consider the path measure of several test particles scaled as in (4.2). This is denoted by $P^\epsilon(\cdot \mid q_1, p_1, \ldots, q_n, p_n)$ and its expectation by $E^\epsilon(\cdot \mid q_1, p_1, \ldots, q_n, p_n)$. We assume that several test particles move asymptotically independently even when started at nearby distances:

Assumption C. Let $b_j(t)$, $j = 1, \ldots, n$, be n independent Brownian motions in R^3 with covariance $2Dt$. Let $q_j^\epsilon(0) = q + \epsilon q_j$. Then for $n = 1, 2, \ldots,$

$$(q_1^\epsilon(t), \ldots, q_n^\epsilon(t)) \to (q + b_1(t), \ldots, q + b_n(t)) \tag{7.3}$$

independently of $q_1, \ldots, q_n$ as $\epsilon \to 0$, in the sense of weak convergence of the path measures $P^\epsilon(\cdot \mid q + \epsilon q_1, p_1, \ldots, q + \epsilon q_n, p_n)$ on $C(R, R^{3n})$.

It follows from the clustering of the equilibrium correlation functions that, as $\epsilon \to 0$,

$$\rho_{\mathrm{eq},2}^\epsilon(\epsilon^{-1} q_1, p_1, \epsilon^{-1} q_2, p_2) \to \rho h_\beta(p_1) \rho h_\beta(p_2) \tag{7.4}$$

except at points of spatial coincidence. If we invoke Assumption C in the case of two test particles starting at $\epsilon^{-1}q_1$, and $\epsilon^{-1}q_2$, then

$$\lim_{\epsilon\to 0}\rho_2^\epsilon(x_1,\sigma_1,x_2,\sigma_2,t)=\prod_{j=1}^{2}h_\beta(p_j)\rho g(q_j,\sigma_j,t) \tag{7.5}$$

for $q_1\neq q_2$. This factorization means that the fluctuations tend to zero as $\epsilon\to 0$, i.e.,

$$\lim_{\epsilon\to 0}\epsilon^3 n^\epsilon(\Delta,\sigma,t)=\int_\Delta dq\,\rho g(q,\sigma,t) \tag{7.6}$$

in probability. By the same argument (7.6) holds also for the steady state [with $g(q,\sigma,t)$ replaced by $g(q,\sigma)$]. It follows then that the higher correlation functions also have to factorize almost surely. Therefore, if two test particles starting at macroscopically distinct points asymptotically move independently, then the color profile becomes deterministic in the hydrodynamic limit. If this property fails, then there are correlations of colors on a macroscopic scale.

To obtain information about the distribution of the color random field one has to consider

$$\epsilon^{3/2}\left[n^\epsilon(\Delta,\sigma,t)-\langle n^\epsilon(\Delta,\sigma,t)\rangle\right] \tag{7.7}$$

which describes the deviations of the color field from its average. It is expected that the distribution of (7.7) tends to a Gaussian as $\epsilon\to 0$. We do not see how the covariance of the limiting fluctuation field could be deduced from the Assumptions made so far.

A different direction of refinement is to study the local (on the macroscopic scale) distribution of colors. One considers then the number of particles, $n^\epsilon(q,t;\Delta,\sigma)$, of color σ in the region $\epsilon^{-1}q+\Delta$ at time $\epsilon^{-2}t$. Note that the reference point q is kept fixed on the macroscopic scale and that the region Δ is independent of ϵ. The collection of random variables $\{n^\epsilon(q,t;\Delta,\sigma)\,|\,\Delta \text{ bounded}\}$ define the local state at q at time t. Its limit as $\epsilon\to 0$ is most easily investigated through the moments of $n^\epsilon(q,t;\Delta,\sigma)$, i.e., through correlation functions. To be specific let us discuss the steady state. The time-dependent states follow the same pattern.

The correlation functions of the local state at q are defined by

$$\begin{aligned}
&\rho_n^\epsilon(x_1,\sigma_1,\ldots,x_n,\sigma_n;q)\\
&\quad=\rho_n\left(\epsilon^{-1}q+q_1,p_1,\sigma_1,\ldots,\epsilon^{-1}q+q_n,p_n,\sigma_n;\epsilon^{-1}L\right)\\
&\quad=\rho_{\mathrm{eq},n}(q_1,p_1,\ldots,q_n,p_n)\\
&\qquad\times P^\epsilon\left(\bigtimes_{j=1}^{n}A(\sigma_j)\,|\,q+\epsilon q_1,-p_1,\ldots,q+\epsilon q_n,-p_n\right)
\end{aligned} \tag{7.8}$$

We used here the translation invariance of the equilibrium state. Making Assumption C, then yields

$$\lim_{\epsilon \to 0} \rho_n^{\epsilon}(x_1, \sigma_1, \ldots, x_n, \sigma_n; q) = \rho_{\mathrm{eq},n}(x_1, \ldots, x_n) \prod_{j=1}^{n} g_s(q, \sigma_j) \qquad (7.9)$$

Therefore, locally at q, one sees an infinite system of particles which have independently of each other color σ with probability $g_s(q, \sigma)$. The system of colored particles is locally in equilibrium with the parameters ρ, β, $g_s(q, \sigma)$. (Presumably, the state with independent coloring is the only time-invariant state with the property that the particles, disregarding their color, are in equilibrium.)

8. CONCLUDING REMARKS

(i) It is very difficult to prove or disprove the validity of the successively stronger Assumptions A, B, C for any real system. We do not even know at the present time whether there are any physical systems for which A but not B is satisfied. It is, however, easy to construct mathematical examples where this is true. In the physics literature only A is generally considered explicitly but in fact B is implicitly assumed to hold.

We briefly describe two of the better understood models (cf. also Ref. 3 for the dilute gas case for which the appropriately modified Assumptions A, B, and C hold).

(a) Assumption B is true for hard rods in one dimension with a general velocity distribution.[11] Since in this model particles cannot pass each other Assumption C cannot hold. In fact,

$$\left[q_1^{\epsilon}(t), q_2^{\epsilon}(t) \right] \to \left[q_1 + b(t), q_2 + b(t) \right]$$

as $\epsilon \to 0$.[12] To have a model which is less trivial as regards B we investigate in Ref. 4 a system of hard rods, where the rods have some probability to pass through each other. C still does not hold.

(b) A higher-dimensional system for which Assumptions A and B are proved to be valid is the periodic Lorentz gas.[13] This is a system of independent particles in two dimensions which move with speed one through a periodic configuration of strictly convex, specularly reflecting scatterers. It is assumed that the distance between two successive collisions is uniformly bounded. A test particle is now simply a single particle moving through the scatterers. If the initial conditions of the test particle are fixed, then there is only a single path and convergence to Brownian motion is not possible. Bunimovich and Sinai prove that, if the initial distribution of the test particle is given by a once differentiable density, then the test particle

process converges weakly to Brownian motion. For the Lorentz gas Assumption C is trivially satisfied, since particles are independent.

(ii) Consider the first example in Section 2. In the initial state we have, using (4.5),

$$\rho_1(q_1, p_1, \sigma_1, t=0) = h_\beta(p_1)\rho n(q_1, \sigma_1, t=0)$$

$$\rho_2(q_1, p_1, \sigma_1, q_2, p_2, \sigma_2, t=0) = h_\beta(p_1)h_\beta(p_2)\rho^2 g(|q_1 - q_2|) \times h(q_1, \sigma_1, t=0)n(q_2, \sigma_2, t=0), \ldots \tag{8.1}$$

where $g(r)$ is the equilibrium radial distribution function of the fluid and $n(q, \sigma, t=0) = (1-\sigma)\theta(q_x) + \sigma[1-\theta(q_x)]$ with $\theta(q_x)$ the Heaviside step function. The time evolution of these correlation functions, $\rho_l(q_1, p_1, \sigma_1, \ldots, q_l, p_l, \sigma_l, t)$, $l = 1, 2, \ldots,$ will be governed by the solution of the infinite BBGKY hierarchy.[5] The black color flux at position q at any time t is given by

$$j(q,t) = \int dp\, p\rho_1(q, p, 1, t) \tag{8.2}$$

In particular, $j(q,0) \equiv 0$, and for a fixed (microscopic) time $t > 0$ the correlations and current will be some complicated functions of t.

A simpler picture emerges on the macroscopic scale. When our assumptions hold, then

$$\lim_{\epsilon\to 0} \rho_1(q_1, p_1, \sigma_1, \epsilon^{-2}t) = \tilde{\rho}_1(q_1, p_1, \sigma_1, t) \equiv h_\beta(p_1)\rho n(0, \sigma_1, t) \tag{8.3}$$

$$\lim_{\epsilon\to 0} \tilde{\rho}_2(q_1, p_1, \sigma_1, q_2, p_2, \sigma_2, t) \equiv h_\beta(p_1)h_\beta(p_2)\rho^2 g(|q_1 - q_2|)n(0, \sigma_1, t)n(0, \sigma_2, t), \text{ etc.}$$

$$\times \lim_{\epsilon\to 0} \epsilon^{-1} j(q, \epsilon^{-2}t) = \tilde{j}(q,t) \equiv -D\rho \operatorname{grad} n(0, 1, t) \tag{8.4}$$

Here $n(q, \sigma, t)$ is the solution of the diffusion equation with initial condition $n(q, \sigma, t=0)$ and $n(0, \sigma, t) = 1/2$. In particular, $\tilde{j}(q,t)$ does not vanish as $t \to 0$. [Because of the singularity in $\operatorname{grad} n(q, \sigma, t=0)$ at $q = 0$ $\tilde{j}(q,t)$ becomes actually infinite as $t \to 0$.] The scaled current is therefore *not* given as an expectation value of a microscopic current in the local equilibrium state. This is of course natural since $j \sim \epsilon\tilde{j}$ and we have taken $\epsilon \to 0$.

In order to get $\tilde{j}$ as an expectation we have to obtain the correlation functions to the next order in an expansion in ϵ, i.e.,

$$\rho_l(q_1, p_1, \sigma_1, \ldots, q_l, p_l, \sigma_l, \epsilon^{-2}t) = \tilde{\rho}_l(q_1, p_1, \sigma_1, \ldots, q_l, p_l, \sigma_l, t) + \epsilon\rho_l^{(1)}(q_1, p_1, \sigma_1, \ldots, q_l, p_l, \sigma_l, t) + \cdots \tag{8.5}$$

and then average the microscopic current,

$$\tilde{j}(q,t) = \int dp\, p\rho_1^{(1)}(q,p,1,t) \tag{8.6}$$

The equality of the right-hand sides of (8.4) and (8.6) is guaranteed by our derivation of Fick's law.

The situation here is entirely analogous to that encountered in the well-known normal, Hilbert, or Chapman–Enskog solutions of the (linear) Boltzmann equation.[5] In that case one deals solely with the one-particle distribution function, while here one deals with the whole state, containing correlations of all orders. In both cases, however, it is the hydrodynamic equations for the conserved quantities which describe the evolution of the system on the slowest time scale that determine the structure of the system on the macroscopic scale.

(iii) The types of initial states described by Eq. (4.5) in which the color depends solely on the particles position can be generalized in an obvious way by having g depend also on v. Assumptions A to C have then to be generalized to include convergence to Brownian motion of the test particles started with any initial velocity. Just how general initial conditions we can allow and still expect the diffusion equation to hold for the color profile is an open question.

(iv) It is possible to consider more general color processes than those discussed in this paper, e.g., we can make color a continuous variable which is conserved but gets redistributed according to some rule when two particles collide. The color profile would then satisfy more general types of linear equations—we shall consider some of these in a later publication.

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