On the Linearity of the Self-Diffusion Process

William W. Wood[1,2] **and Jerome J. Erpenbeck**[1,3]

Formal arguments are given that the self-diffusion process, understood as the mutual diffusion process in a system which consists of two mechanically similar species of particles, and which is at total equilibrium if the species labels are ignored, is an inherently linear, but nonlocal, transport process. There are no nonlinear Burnett effects, and the nonlocal diffusion coefficient is independent of the composition of the mixture. The present state of knowledge, from theory and from computer experiments, concerning the various quantities which appear in the formal analysis is summarized for both fluid and Lorentz systems.

1. INTRODUCTION

Some years ago, at a time when the existence and significance of the long-time tails of the velocity autocorrelation function and the other transport time correlation functions were still somewhat controversial, Professor E. G. D. Cohen asked us whether it would be possible to directly simulate a self-diffusion process on a computer, the objective being to compute the diffusion coefficient as a ratio of current to gradient (in a fashion similar to the experimental measurement of a diffusion coefficient in a diffusion cell), and then to compare the result with the usual integral of the velocity autocorrelation function. This suggestion was motivated by questions that had been raised as to whether the long-time tails were properly to be included in the time integral, or somehow "renormalized" away. It was easy enough to see how a transient self-diffusion process could be simulated, but it rapidly became clear that the computer "experiment"

---

was unnecessary, since the self-diffusion process was amenable to an exact (at the formal level) theoretical analysis; we present this in Section 2 (an abbreviated account was given in a lecture by one of us[1]).

The present discussion is motivated also by the remark by Lebowitz and Spohn[2] regarding the desirability of obtaining rigorous justifications of the time-correlation function formulas for the transport coefficients, even at the purely formal level (i.e., omitting proofs of the existence of various limits, etc.). The self-diffusion process is surely the simplest transport process, and one would expect that an exact (formal) derivation would be relatively easy. Such a discussion has in fact been given by Dorfman[3] (see also Berne[4]) for the case of a single "tagged" particle moving in a system of $N - 1$ mechanically similar, untagged particles. The diffusion coefficient was indeed found to be related to the velocity autocorrelation function in the usual way. The previously derived[5] time correlation function expression for the super-Burnett self-diffusion coefficient was also obtained, giving a flux contribution which is linear in the third-order gradient of the number density. This discussion, however, seemed to leave open the possibility that other effects might appear when the concentration of tagged particles was noninfinitesimal, due to "correlations" among the tagged particles. In particular, was it possible that the self-diffusion coefficient would depend upon the concentration of tagged particles? Might it depend upon the gradient of the tagged particle concentration, i.e., were nonlinear effects possible in the self-diffusion process? The common belief certainly has been in the negative, in both cases, but a detailed proof has been lacking; see, for example, the remarks in this connection by Ernst *et al.*[6] Standard linear response methods have been used by Dufty,[7] with the same results, but such methods of course leave unanswered the question of nonlinear effects, as well as being subject to the general objections raised against linear response theory by van Kampen.[8]

The analysis in Section 2 considers the general case, both in regard to the tagged particle concentration and the possibility of nonlinear effects, and it answers both of these questions in the negative. However, it is open to the possible objection that the assumed initial state is not a "local equilibrium" state. Because of the importance of a correct treatment of fluctuations in the theory of transport, we give in Section 3 an alternative derivation which starts from a local equilibrium state constructed by the imposition of external potential fields which act differently upon the two species of particles, and which are switched off at $t = 0$. The results are unchanged.

Finally, in Section 4 we conclude with a summary of what seems to be known, from theoretical analysis and computer experiments, about the existence of the various limits which are of interest in the formal analysis.

It is important to begin by specifying exactly what we mean by a self-diffusion process. First, we regard self-diffusion as the special case of mutual diffusion between two species[4] of particles which are mechanically identical, differing only in their species labels (1 and 2). We use classical (rather than quantum) statistical mechanics throughout. Second, in order to exclude the simultaneous occurrence of other transport processes, we choose the initial state so that throughout the process the system will be in a state of uniform equilibrium if the species labels are ignored. In particular, then, all quantities which are independent of the species labels, such as the total number density, the pressure, the temperature, etc., are required to be constant as functions both of the position within the system and of the time. Subject to these conditions, we sample the initial state from some specified ensemble in which the individual number densities n_i, $i = 1$ or 2, of the two species are, on the average, nonuniform as a function of position. We then follow the evolution of these number densities for $t > 0$ under the natural dynamics of the system in which the forces among the particles are independent of the labels (mechanical similarity), and enquire as to the relation between the diffusion current of one species (say 1) and its number density gradient. These definitions are essentially those used by Raveche and Mayer.[9]

We will consider through most of the discussion finite d-dimensional systems of volume V under periodic boundary conditions. Some further discussion of this point is given in the Appendix.

2. INITIAL GRADIENTS PRODUCED BY RANDOM LABELING

Our first method of producing the initial state proceeds in two steps:

Step 1. The initial phase $\Gamma_N = \{\mathbf{p}^N, \mathbf{q}^N\}$, where $\mathbf{p}^N = \{\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\}$ and $\mathbf{q}^N = \{\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N\}$ denote the momenta and positions of the N particles,[5] is selected from the canonical (or microcanonical) ensemble for specified values of the ensemble parameters N, V, and temperature T (or N, V, and energy E).

Step 2. Each particle $\alpha = 1, 2, \ldots, N$ is independently of the others labeled as species 1 with a given probability $P_1(\mathbf{q}_\alpha)$ depending upon its position $\mathbf{q}_\alpha$, or as species 2 with probability $P_2(\mathbf{q}_\alpha) = 1 - P_1(\mathbf{q}_\alpha)$.

The system is then allowed to evolve under its equations of motion and the specified boundary condition for times $t > 0$. By assumption the

---

[4] For simplicity of notation we consider a binary mixture; there is no difficulty in extending the discussion to more than two components.

[5] We use the notation appropriate to a system of point particles, but the argument would apply equally well to a system of structured particles.

particle motions are independent of the labeling, and by construction the system is at equilibrium (in the ensemble sense) if the species labeling is ignored. However, it is not at equilibrium with respect to the species number densities [unless $P_1(\mathbf{q})$ is independent of $\mathbf{q}$], and we expect that a transient self-diffusion process will occur in which the number densities approach uniformity as $t \to \infty$.

The number density $n_1(\mathbf{r}, t)$ of species 1 at the position $\mathbf{r}$ at time t is given by

$$n_1(\mathbf{r}, t) = \left\langle \sum_{i=1}^{N} \sum_{\nu} \delta\left[\mathbf{r} - \nu L - \mathbf{q}_i(t)\right] P_1(\mathbf{q}_i) \right\rangle \tag{1}$$

in which $\delta(\mathbf{r})$ is the d-dimensional Dirac delta function, and the angular brackets denote the statistical mechanical average over the initial phase Γ_N in the ensemble used in Step 1 of the initial preparation. We follow the convention that the unadorned phase variables (e.g., Γ_N, $\mathbf{p}^N$, $\mathbf{q}_i$, etc.) denote initial values, with values at a later time t [e.g., $\Gamma_N(t)$, $\mathbf{p}^N(t)$, $\mathbf{q}_i(t)$, etc.] being explicitly so notated. We follow the "infinite checkerboard" interpretation of periodic boundary conditions discussed in the Appendix, with $L = V^{1/d}$ denoting the period of the system.[6] The integration over the initial positions $\mathbf{q}_i$ is restricted to the reference cell $\nu = 0$, and $\mathbf{q}_i(t)$ denotes the position of particle i at time t (not necessarily in cell 0) given that it was initially at $\mathbf{q}_i$. The sum over $\nu = (\nu_1, \nu_2, \ldots, \nu_d)$ is a d-fold summation over all positive, negative, and zero integer values of the cell indices ν_i. Note that, for fixed values of $\mathbf{r}$ (not necessarily in cell 0), i, t, and Γ_N, the argument of the delta function will vanish for at most a single value of the index ν. It is evident that $n_1(\mathbf{r}, t)$ is a periodic function of the position $\mathbf{r}$. It is important to note that the ensemble probability density whose use is signified by the angular brackets is independent of the species labeling, and is symmetrical in all the particle indices. The factor $P_1(\mathbf{q}_i)$ accounts for the stochastic character of Step 2 of the initial preparation.

At $t = 0$ Eq. (1) reduces, with use of the translational invariance of the periodic system, to

$$n_1(\mathbf{r}, 0) = nP_1(\mathbf{r}) \tag{2}$$

with $n = N/V$ denoting the (uniform) total number density. If we introduce into Eq. (1) an additional delta function and a compensating integration (over the volume V) and eliminate P_1 in favor of $n_1(\mathbf{r}, 0)$ by use of Eq. (2), we can write it in the form

$$n_1(\mathbf{r}, t) = \int d\mathbf{r}' \, n_1(\mathbf{r}', 0) G_s(\mathbf{r} - \mathbf{r}', t) \tag{3}$$

---

[6] The notation is easily adapted to accommodate cases in which the period of the system is different in different directions.

where we have introduced the van Hove[10] self-correlation function

$$G_s(\mathbf{r} - \mathbf{r}', t) = V \left\langle \sum_{\nu} \delta[\mathbf{r} - \nu L - \mathbf{q}_1(t)] \delta[\mathbf{r}' - \mathbf{q}_1] \right\rangle$$

$$= n^{-1} \left\langle \sum_{i=1}^{N} \sum_{\nu} \delta[\mathbf{r} - \nu L - \mathbf{q}_i(t)] \delta[\mathbf{r}' - \mathbf{q}_i] \right\rangle$$

$$= \left\langle \sum_{\nu} \delta[\mathbf{r} - \mathbf{r}' - \nu L - \Delta\mathbf{q}_1(t)] \right\rangle \tag{4}$$

In doing so, we have used the above-mentioned symmetry of the ensemble probability and again the translational invariance of the periodic system. $\Delta\mathbf{q}_1(t) = \mathbf{q}_1(t) - \mathbf{q}_1$ is the displacement of the representative particle 1. Note that it does not matter whether particle 1 was labeled as species 1 or as species 2 in Step 2 of the initial preparation, inasmuch as the angular brackets refer to the average over the ensemble used in Step 1.

In the same way we can write the diffusion current of species 1 as

$$\mathbf{J}_1(\mathbf{r}, t) = \left\langle \sum_{i=1}^{N} \mathbf{v}_i(t) \sum_{\nu} \delta[\mathbf{r} - \nu L - \mathbf{q}_i(t)] P_1(\mathbf{q}_i) \right\rangle \tag{5}$$

$$= \int d\mathbf{r}' \, n_1(\mathbf{r}', 0) \mathbf{H}_s(\mathbf{r} - \mathbf{r}', t) \tag{6}$$

with

$$\mathbf{H}_s(\mathbf{r} - \mathbf{r}', t) = V \left\langle \mathbf{v}_1(t) \sum_{\nu} \delta[\mathbf{r} - \nu L - \mathbf{q}_1(t)] \delta[\mathbf{r}' - \mathbf{q}_1] \right\rangle$$

$$= \left\langle \mathbf{v}_1(t) \sum_{\nu} \delta[\mathbf{r} - \mathbf{r}' - \nu L - \Delta\mathbf{q}_1(t)] \right\rangle \tag{7}$$

in which $\mathbf{v}_i(t)$ denotes the velocity of particle i at time t.

It is clear from the convolution form of Eqs. (3) and (6) that it will be advantageous to introduce Fourier transforms

$$\tilde{f}(\mathbf{k}, t) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) f(\mathbf{r}, t) \tag{8}$$

whereupon these equations become

$$\tilde{n}_1(\mathbf{k}, t) = \tilde{n}_1(\mathbf{k}, 0) \tilde{G}_s(\mathbf{k}, t)$$
$$\tilde{\mathbf{J}}_1(\mathbf{k}, t) = \tilde{n}_1(\mathbf{k}, 0) \tilde{\mathbf{H}}_s(\mathbf{k}, t) \tag{9}$$

with

$$\tilde{G}_s(\mathbf{k}, t) = \left\langle \exp[i\mathbf{k} \cdot \Delta\mathbf{q}_1(t)] \right\rangle$$
$$\tilde{\mathbf{H}}_s(\mathbf{k}, t) = \left\langle \mathbf{v}_1(t) \exp[i\mathbf{k} \cdot \Delta\mathbf{q}_1(t)] \right\rangle \tag{10}$$

We note that $\tilde{G}_s(\mathbf{k}, t)$ is the "self" part of the intermediate scattering function,[4] and that

$$\frac{\partial}{\partial t} \tilde{G}_s(\mathbf{k}, t) = i\mathbf{k} \cdot \tilde{\mathbf{H}}_s(\mathbf{k}, t) \tag{11}$$

Wavelength- and Time-Dependent Diffusion Coefficient

For a classical Fick's law diffusion process obeying

$$\mathbf{J}(\mathbf{r}, t) = - D \frac{\partial}{\partial \mathbf{r}} n(\mathbf{r}, t) \tag{12}$$

with a *constant* diffusion coefficient D, we have after Fourier transformation

$$\tilde{\mathbf{J}}(\mathbf{k}, t) = i k D \tilde{n}(\mathbf{k}, t) \tag{13}$$

Solving this for D we obtain

$$D = \frac{- i \mathbf{k} \cdot \tilde{\mathbf{J}}(\mathbf{k}, t)}{k^2 \tilde{n}(\mathbf{k}, t)} \tag{14}$$

From Eqs. (9) we see, for the self-diffusion process considered here, that the $\mathbf{k}$ and t dependence of $\tilde{\mathbf{G}}_s$ and $\tilde{\mathbf{H}}_s$ will not result in a *constant* diffusion coefficient. By analogy we accordingly define a wavelength- and time-dependent diffusion coefficient

$$\tilde{D}(\mathbf{k}, t) = \frac{- i \mathbf{k} \cdot \tilde{\mathbf{J}}_1(\mathbf{k}, t)}{k^2 \tilde{n}_1(\mathbf{k}, t)} \tag{15}$$

With use of Eqs. (9) and (11), we can write this as

$$\tilde{D}(\mathbf{k}, t) = \frac{- i \mathbf{k} \cdot \tilde{\mathbf{H}}_s(\mathbf{k}, t)}{k^2 \tilde{G}_s(\mathbf{k}, t)} \tag{16}$$

$$= - \frac{1}{k^2} \frac{\partial}{\partial t} \ln \tilde{G}_s(\mathbf{k}, t) \tag{17}$$

To this point our analysis and definitions apply without approximation to a finite periodic system. If we now consider the case of an isotropic fluid in the thermodynamic limit ($L \to \infty$, N/V = constant), it is not difficult to show that $\tilde{\mathbf{H}}_s(\mathbf{k}, t)$ becomes a vector in the direction of $\mathbf{k}$. Then we can write

$$\tilde{\mathbf{H}}_s(\mathbf{k}, t) = \frac{\mathbf{k} \cdot \tilde{\mathbf{H}}_s(\mathbf{k}, t)}{k^2} \mathbf{k} = i \mathbf{k} \tilde{G}_s(\mathbf{k}, t) \tilde{D}(\mathbf{k}, t) \tag{18}$$

using Eq. (16). Multiplication by $n_1(\mathbf{k}, 0)$ and use of Eqs. (9) leads to

$$\tilde{\mathbf{J}}_1(\mathbf{k}, t) = i \mathbf{k} \tilde{n}_1(\mathbf{k}, t) \tilde{D}(\mathbf{k}, t) \tag{19}$$

Assuming the existence of the inverse Fourier transform $D(\mathbf{r}, t)$ of $\tilde{D}(\mathbf{k}, t)$, this is equivalent to

$$\mathbf{J}_1(\mathbf{r}, t) = - \int d\mathbf{r}' \, D(\mathbf{r} - \mathbf{r}', t) \frac{\partial}{\partial \mathbf{r}'} n_1(\mathbf{r}', t) \tag{20}$$

From this we see that in the thermodynamic limit the inverse Fourier transform $D(\mathbf{r}, t)$ of the wavelength- and time-dependent diffusion coeffi-

cient $\tilde{D}(\mathbf{k},t)$ given by Eq. (17) is a temporally local, spatially nonlocal diffusion coefficient.

From Eqs. (10) and (17) the formal k expansion

$$\tilde{D}(\mathbf{k},t) = D^{(0)}(t) - k^2 D^{(2)}(t) + \cdots \tag{21}$$

follows easily, with

$$D^{(0)}(t) = \frac{1}{2}\frac{\partial}{\partial t}\left\langle \Delta x_1(t)^2 \right\rangle \tag{22}$$

$$D^{(2)}(t) = \frac{1}{4!}\frac{\partial}{\partial t}\left[\left\langle \Delta x_1(t)^4 \right\rangle - 3\left\langle \Delta x_1(t)^2 \right\rangle^2 \right] \tag{23}$$

assuming the isotropy of an infinite fluid, and writing $\Delta x_1(t)$ for the x component of $\Delta \mathbf{q}_1(t)$. Substitution of Eq. (21) into Eq. (19) followed by inverse Fourier transformation leads to the gradient expansion of the spatial nonlocality in Eq. (20), i.e.,

$$\mathbf{J}_1(\mathbf{r},t) = -D^{(0)}(t)\frac{\partial}{\partial \mathbf{r}}n_1(\mathbf{r},t) - D^{(2)}(t)\frac{\partial}{\partial \mathbf{r}}\left[\frac{\partial}{\partial \mathbf{r}}\cdot\frac{\partial}{\partial \mathbf{r}}n_1(\mathbf{r},t) \right] - \cdots \tag{24}$$

with $D^{(0)}(t)$ corresponding to the time-dependent generalization of the usual diffusion coefficient, and $D^{(2)}(t)$ to a similar generalization of the super-Burnett diffusion coefficient. From Eq. (22) the familiar expression

$$D^{(0)}(t) = \int_0^t dt' \left\langle v_{1x}(0)v_{1x}(t') \right\rangle \tag{25}$$

giving $D^{(0)}(t)$ in terms of the velocity autocorrelation function follows easily, while with somewhat more labor[3,5] the super-Burnett coefficient can be expressed in terms of a "four-point" velocity autocorrelation function

$$D^{(2)}(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3\, c^{(2)}(t_1,t_2,t_3)$$

$$c^{(2)}(t_1,t_2,t_3) = \left\langle v_{1x}(0)v_{1x}(t_1)v_{1x}(t_2)v_{1x}(t_3) \right\rangle \tag{26}$$

$$- \sum_P \left\langle v_{1x}(0)v_{1x}(t_1) \right\rangle\left\langle v_{1x}(t_2)v_{1x}(t_3) \right\rangle$$

In these equations $v_{1x}(t)$ denotes the x component of the velocity of particle 1, and in the last equation the sum is over the three distinct permutations of the t_1, t_2, and t_3 variables.

Wavelength- and Epsilon-Dependent Diffusion Coefficient

As is well known, one can also obtain a further generalization of Fick's law involving a diffusion coefficient which is nonlocal in both space and

time. We give the derivation in order to provide a basis for the discussion of some recent developments in Section 4. Returning to the classical Fick's law Eq. (13) and denoting Laplace transforms by

$$\hat{f}(\mathbf{k}, \epsilon) = \int_0^\infty dt\, e^{-\epsilon t} \tilde{f}(\mathbf{k}, t) \tag{27}$$

we have

$$\hat{\mathbf{J}}(\mathbf{k}, \epsilon) = ik D \hat{n}(\mathbf{k}, \epsilon) \tag{28}$$

from which

$$D = \frac{-i\mathbf{k} \cdot \hat{\mathbf{J}}(\mathbf{k}, \epsilon)}{k^2 \hat{n}(\mathbf{k}, \epsilon)} \tag{29}$$

By analogy again we are led to define a wavelength- and epsilon-dependent diffusion coefficient

$$\hat{\mathcal{D}}(\mathbf{k}, \epsilon) = \frac{-i\mathbf{k} \cdot \hat{\mathbf{J}}_1(\mathbf{k}, \epsilon)}{k^2 \hat{n}_1(\mathbf{k}, \epsilon)} \tag{30}$$

We use the notation $\hat{\mathcal{D}}(\mathbf{k}, \epsilon)$ [rather than $\hat{D}(\mathbf{k}, \epsilon)$] to emphasize that it is *not* the Laplace transform of $\tilde{D}(\mathbf{k}, t)$. Taking the Laplace transforms of Eqs. (9) gives

$$\hat{n}_1(\mathbf{k}, \epsilon) = \tilde{n}_1(\mathbf{k}, 0) \hat{G}_s(\mathbf{k}, \epsilon)$$
$$\hat{\mathbf{J}}_1(\mathbf{k}, \epsilon) = \tilde{n}_1(\mathbf{k}, 0) \hat{\mathbf{H}}_s(\mathbf{k}, \epsilon) \tag{31}$$

with the use of which Eq. (30) becomes

$$\hat{\mathcal{D}}(\mathbf{k}, \epsilon) = \frac{-i\mathbf{k} \cdot \hat{\mathbf{H}}_s(\mathbf{k}, \epsilon)}{k^2 \hat{G}_s(\mathbf{k}, \epsilon)} \tag{32}$$

Using Eqs. (11) and (10) we have

$$i\mathbf{k} \cdot \hat{\mathbf{H}}_s(\mathbf{k}, \epsilon) = \int_0^\infty dt\, e^{-\epsilon t} \frac{\partial}{\partial t} \tilde{G}_s(\mathbf{k}, t) = \epsilon \hat{G}_s(\mathbf{k}, \epsilon) - 1 \tag{33}$$

which permits Eq. (32) to be written in the familiar form[4]

$$\hat{\mathcal{D}}(\mathbf{k}, \epsilon) = \frac{1 - \epsilon \hat{G}_s(\mathbf{k}, \epsilon)}{k^2 \hat{G}_s(\mathbf{k}, \epsilon)} \tag{34}$$

of the wavelength- and epsilon-dependent diffusion coefficient of generalized hydrodynamics. For an isotropic fluid, which we assume in the large system limit, $\hat{\mathbf{H}}_s(\mathbf{k}, \epsilon)$ will be a vector in the direction of $\mathbf{k}$, and Eq. (30) can be written as

$$\hat{\mathbf{J}}_1(\mathbf{k}, \epsilon) = ik\hat{n}_1(\mathbf{k}, \epsilon)\hat{\mathcal{D}}(\mathbf{k}, \epsilon) \tag{35}$$

Taking both inverse transforms gives

$$\mathbf{J}_1(\mathbf{r}, t) = -\int_0^t dt' \int d\mathbf{r}' \, \mathcal{D}(\mathbf{r} - \mathbf{r}', t - t') \frac{\partial}{\partial \mathbf{r}'} n_1(\mathbf{r}', t) \tag{36}$$

thus identifying the inverse Laplace-inverse Fourier transform $\mathcal{D}(\mathbf{r}, t)$ of $\hat{\mathcal{D}}(\mathbf{k}, \epsilon)$ as a spatially and temporally nonlocal diffusion coefficient.

Alternatively, by substituting for $G_s(\mathbf{k}, \epsilon)$ in Eq. (34) using Eq. (31), rearranging, and taking only the inverse Laplace transform, we obtain

$$\frac{\partial}{\partial t} \tilde{n}_1(\mathbf{k}, t) = -k^2 \int_0^t dt' \, \tilde{\mathcal{D}}(\mathbf{k}, t - t') \tilde{n}_1(\mathbf{k}, t') \tag{37}$$

From dynamical reversibility and Eq. (10) we have

$$\tilde{G}_s(\mathbf{k}, t) = \left\langle \cos\left[\mathbf{k} \cdot \Delta\mathbf{q}_1(t)\right] \right\rangle \tag{38}$$

from which we see that, again assuming isotropy, the $\mathbf{k}$ expansion of $G_s(\mathbf{k}, t)$, and therefore that of $\tilde{\mathcal{D}}(\mathbf{k}, t)$, will contain only even powers of k. Substituting

$$\tilde{\mathcal{D}}(\mathbf{k}, t) = \sum_{n=0}^{\infty} (-1)^n \tilde{\mathcal{D}}^{(2n)}(t) k^{2n} \tag{39}$$

into Eq. (37) and taking the inverse Fourier transform, we have

$$\frac{\partial}{\partial t} n_1(\mathbf{r}, t) = \sum_{n=0}^{\infty} \int_0^t dt' \, \tilde{\mathcal{D}}^{(2n)}(t - t') \left(\frac{\partial}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} \right)^{n+1} n_1(\mathbf{r}, t') \tag{40}$$

This temporally nonlocal gradient or Burnett expansion is the one discussed by Alley and Alder,[11] and as they showed, one easily finds for the first two coefficients

$$\tilde{\mathcal{D}}^{(0)}(t) = \left\langle v_{1x}(0) v_{1x}(t) \right\rangle \tag{41}$$

$$\tilde{\mathcal{D}}^{(2)}(t) = \frac{1}{4!} \left[\frac{\partial}{\partial t} \right]^2 \left\langle \Delta x_1(t)^4 \right\rangle - \frac{\partial}{\partial t} \int_0^t dt' \, D^{(0)}(t - t') D^{(0)}(t') \tag{42}$$

where $D^{(0)}(t)$ is given by Eq. (25) and also by

$$D^{(0)}(t) = \int_0^t dt' \, \tilde{\mathcal{D}}^{(0)}(t') \tag{43}$$

Summary

As was already emphasized, the above results are the same as those usually obtained by considering the case of a single tagged particle in a system of $N - 1$ mechanically similar particles. Here, however, we have considered a system containing an arbitrary number $N_1 = \int d\mathbf{r} \, n_1(\mathbf{r}, t)$ of particles of species 1 initially distributed nonuniformly over the volume V, together with $N_2 = N - N_1$ particles of species 2 similarly distributed, with

the overall number density n being uniform both initially and throughout the diffusion process. We find that the wavelength- and time-dependent diffusion coefficient is given by the usual expression involving only the van Hove self-correlation function of the unlabeled, homogeneous system. From this it follows that the diffusion coefficient is independent of the relative number densities of the two species. Furthermore, it is independent of the gradient of the number density [note also the linearity of Eq. (20)], so that there are no nonlinear Burnett effects. These results were quite generally expected, but as far as we are aware they have not previously been explicitly demonstrated.

3. INITIAL GRADIENTS PRODUCED BY EXTERNAL FIELDS

It is possible to question whether the simple results obtained in Section 2 are attributable to the rather special character of the preparation of the initial state. Accordingly, in this section we show that the same results are obtained by starting from a "local equilibrium" initial state, in the spirit of the usual "linear response" theory. However, the important feature of the discussion will be the fact that we do not linearize at any stage of the analysis.

We suppose that the initial state is sampled from the grand canonical ensemble for a system of two species which are mechanically identical except for the presence of two external potential fields $u_1(\mathbf{r})$ and $u_2(\mathbf{r})$, with $u_1(\mathbf{r})$ acting only on the particles of species 1 and $u_2(\mathbf{r})$ only on those of species 2. At this point the two external fields are arbitrary periodic functions of $\mathbf{r}$, but we will shortly see how they must be constrained in order to satisfy our requirement that the initial state be an equilibrium state when the species labels are ignored. We imagine that, after the initial state is prepared in this fashion, the external fields are switched off at $t = 0$, and the system is allowed to evolve from this state according to its field-free Hamiltonian. The latter, according to our assumption of the mechanical similarity of the two species, is symmetrical in the indices of all the (fluctuating, among different initial states) $N = N_1 + N_2$ particles in the sampled system, with N_i again denoting the fluctuating number of particles of species i.

Under the above assumptions, the number density of species 1 is now given by

$$n_1(\mathbf{r}, t) = \frac{1}{\Xi} \sum_{N_1 = 0}^{\infty} \sum_{N_2 = 0}^{\infty} \frac{z_1^{N_1} z_2^{N_2}}{N_1! \, N_2!} \int d\Gamma_N \, \rho(\Gamma_N)$$

$$\times \exp\left[-\beta \sum_{\alpha_1} u_1(\alpha_1) - \beta \sum_{\alpha_2} u_2(\alpha_2) \right] \sum_{\alpha_1'} \sum_{\nu} \delta\left[\mathbf{r} - \nu L - \mathbf{q}_{\alpha_1'}(t) \right]$$

$$(44)$$

Here $\beta = 1/k_B T$ with k_B the Boltzmann constant. The absolute activity z_i of species i is $\exp(\beta\mu_i)$, where μ_i is the chemical potential. Γ_N denotes the initial phase variables of the $N = N_1 + N_2$ particle system for particular values of N_1 and N_2, and $\rho(\Gamma_N) = \exp[-\beta\mathcal{H}(\Gamma_N)]$ is the corresponding unnormalized canonical ensemble probability density, with $\mathcal{H}(\Gamma_N)$ denoting the field-free Hamiltonian function. The α_1 and α_1' sums run over the particle indices of species 1, the α_2 sum over those of species 2. The notation $u_1(\alpha_1)$ is an abbreviation for $u_1(\mathbf{q}_{\alpha_1})$. The quantity Ξ is the grand canonical partition function

$$\Xi = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \frac{z_1^{N_1} z_2^{N_2}}{N_1! \, N_2!} \int d\Gamma_N \, \rho(\Gamma_N) \exp\left[-\beta\sum_{\alpha_1} u_1(\alpha_1) - \beta\sum_{\alpha_2} u_2(\alpha_2) \right]$$

(45)

For convenience we will number the particles of species 1 from 1 to N_1, those of species 2 from $N_1 + 1$ to $N = N_1 + N_2$. It will be convenient to use the abbreviations

$$e_i(\mathbf{r}) = \exp\left[-\beta u_i(\mathbf{r}) \right] \qquad (i = 1, 2)$$

(46)

Transforming the double summation from N_1 and N_2 to N_1 and N, then changing the order of summation allows Eq. (45) to be written

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int d\Gamma_N \, \rho(\Gamma_N) \sum_{N_1=0}^{N} \binom{N}{N_1} \left[\prod_{\alpha_1} z_1 e_1(\alpha_1) \right]$$
$$\times \left[\prod_{\alpha_2} z_2 e_2(\alpha_2) \right]$$

(47)

The following Lemma is easily proved by induction: Let

$$F_n = \int d\mathbf{x}^n \, \rho(\mathbf{x}^n) \sum_{m=0}^{n} \binom{n}{m} \left[\prod_{i=1}^{m} f_1(\mathbf{x}_i) \right] \left[\prod_{j=m+1}^{n} f_2(\mathbf{x}_j) \right]$$

(48)

with $\mathbf{x}^n = \{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n\}$. If $\rho(\mathbf{x}^n)$ and the integration limits are symmetric in the $\mathbf{x}_i$ variables, then

$$F_n = \int d\mathbf{x}^n \, \rho(\mathbf{x}^n) \prod_{i=1}^{n} \left[f_1(\mathbf{x}_i) + f_2(\mathbf{x}_i) \right]$$

(49)

Using this in Eq. (47) gives

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int d\Gamma_N \, \rho(\Gamma_N) \prod_{\alpha=1}^{N} \left[z_1 e_1(\alpha) + z_2 e_2(\alpha) \right]$$

(50)

We can now immediately see that this will reduce to the grand canonical partition function for a uniform homogeneous system of absolute activity z if we require that the two potential fields satisfy the relation

$$z_1 e_1(\mathbf{r}) + z_2 e_2(\mathbf{r}) = z$$

(51)

with z independent of $\mathbf{r}$. This is the condition for the system to be at equilibrium when the species labels are ignored; we assume in all that follows that it is satisfied.

Equation (44) can be similarly reduced to

$$n_1(\mathbf{r}, t) = \frac{z_1}{z} \int d\mathbf{r}' \, e_1(\mathbf{r}') \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int d\Gamma_N \, \rho(\Gamma_N)$$

$$\times \sum_{\alpha=1}^{N} \sum_{\nu} \delta\big[\mathbf{r} - \nu L - \mathbf{q}_\alpha(t)\big] \delta[\mathbf{r}' - \mathbf{q}_\alpha] \qquad (52)$$

The most convenient definition[7] of the van Hove self-correlation function in the grand canonical ensemble is (using translational invariance)

$$G_s(\mathbf{r} - \mathbf{r}', t) = \frac{1}{\Xi n} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int d\Gamma_N \, \rho(\Gamma_N) \sum_{\alpha=1}^{N} \sum_{\nu} \delta\big[\mathbf{r} - \nu L - \mathbf{q}_\alpha(t)\big] \delta[\mathbf{r}' - \mathbf{q}_\alpha]$$

$$(53)$$

with

$$n = \frac{\overline{N}}{V} = \frac{1}{\Xi V} \sum_{N=0}^{\infty} \frac{z^N}{N!} N \int d\Gamma_N \, \rho(\Gamma_N) \qquad (54)$$

being the average total number density. In these terms we can write Eq. (52) as

$$n_1(\mathbf{r}, t) = \frac{z_1 n}{z} \int d\mathbf{r}' \, e_1(\mathbf{r}') G_s(\mathbf{r} - \mathbf{r}', t) \qquad (55)$$

or with use of the initial conditions as in Section 2,

$$n_1(\mathbf{r}, t) = \int d\mathbf{r}' \, n_1(\mathbf{r}', 0) G_s(\mathbf{r} - \mathbf{r}', t) \qquad (56)$$

which is identical to Eq. (3).

It is clear from the above discussion that the diffusion current, defined now by the right-hand side of Eq. (44) with an additional factor of $\mathbf{v}_{\alpha'_1}(t)$, will correspondingly reduce to Eq. (6), with $\mathbf{H}_s(\mathbf{r} - \mathbf{r}', t)$ now being defined by the right-hand side of Eq. (53) with an additional factor $\mathbf{v}_\alpha(t)$ introduced. All of the subsequent discussion of Section 2 then follows without change, except that the $\langle \cdots \rangle$ are now interpreted as grand canonical averages for the unlabeled, field-free system.

The initial local equilibrium procedure used in this section can also be carried out in the canonical (NVT) ensemble, but at the expense of much more labor. In the course of the analysis the many-particle van Hove

---

[7] The definition is similar to the conventional definition of the equilibrium pair correlation function in the grand canonical ensemble.[12]

correlation functions (both "self" and "distinct") appear, but can be shown to cancel in the thermodynamic limit by use of their factorization properties when two or more groups of particles are widely separated (provided that the asymptotic behavior is approached sufficiently rapidly).

4. DISCUSSION

We have seen, in Sections 2 and 3, that if the initial state of our mixture of two mechanically identical species of particles is sampled from an ensemble which is a total equilibrium ensemble if the species labels are ignored, but which corresponds to nonuniform density distributions of the individual species, then the assumed approach to equilibrium in the individual species densities is governed by the usual generalized hydrodynamics versions of Fick's law involving a wavelength- and time-dependent (or, alternatively, a wavelength- and epsilon-dependent) diffusion coefficient. These transform-space quantities have alternative interpretations in coordinate and time space involving nonlocality in space only, or in both space and time, respectively. These well-known results are usually derived for the case of a single tagged particle moving in a bath of mechanically similar untagged particles. Their derivation here for a general binary mixture of two mechanically similar species, without linearizing in small departures from equilibrium, verifies the common expectation that the self-diffusion coefficient is independent of both the relative number densities of the two components and the magnitude of the gradients. Thus we can indeed assert that self-diffusion is a linear process, but a nonlocal one.[6]

We emphasize that the derivations presented here are formal in nature, inasmuch as we have not considered the questions of the existence of the various transform quantities, or the convergence of the k expansions. It seems appropriate, therefore, to conclude with a brief summary of what seems to be known or indicated by the various theoretical or molecular dynamics ("computer experiments") studies which have been made of the self-diffusion process.

Fluid Systems, Navier–Stokes Transport Coefficients

For nonzero values of k and finite values of t, $\tilde{D}(k, t)$ as given by Eqs. (10) and (17) is expected to be well behaved. Difficulties arise with respect to the long-wavelength and long-time limits, as was first noted by Alder and Wainwright[13] on the basis of molecular dynamics calculations on systems of hard spheres and hard disks. They were also able to explain these results on the basis of a theoretical model involving the use of hydrodynamic equations at a molecular level and applicable to more

general fluid models. These studies indicated that the normalized velocity autocorrelation function

$$\rho_D^{(0)}(t) = \beta m \langle v_{1x}(0) v_{1x}(t) \rangle \tag{57}$$

(with m denoting the mass of a particle) varies asymptotically for large t according to

$$\rho_D^{(0)}(t) \sim \alpha_D^{(0)} t^{-p} \tag{58}$$

with $p = d/2$ ($d = 2$ or 3). The coefficient $\alpha_D^{(0)}$ depends on the density and dimensionality (and on the temperature for non-hard-core systems). As a result, in two-dimensional fluids, the time-dependent self-diffusion coefficient $D^{(0)}(t)$ as given by Eq. (25) diverges in the long-time limit. In three dimensions the integral is convergent, but rather slowly compared to the exponential behavior expected from the Boltzmann equation. The same behavior, with different coefficients $\alpha_\eta^{(0)}$, $\alpha_\lambda^{(0)}$, etc., was found for the other transport coefficients (i.e., the shear viscosity, thermal conductivity, etc.), although with much less precision in the case of the molecular dynamics work. Subsequent molecular dynamics investigations, on both hard-core[1,14–16] and soft-core[17–18] fluid systems have confirmed and extended these early results. These molecular dynamics discoveries have spawned an immense theoretical literature, exemplified by the kinetic theory derivation of Eq. (58) by Dorfman and Cohen[19] and the mode coupling theory of Ernst, Hauge, and van Leeuwen.[20] Since it is not our purpose to give a complete account here, we refer to a number of recent reviews.[21–25]

Within the realm of two- and three-dimensional fluids, the only case known to us which may be an exception to Eq. (58) is the two-dimensional classical electron gas. For this system Hansen et al.[26] found oscillatory behavior of the velocity autocorrelation function out to the longest times investigated in their molecular dynamics calculations. Their estimates of the self-diffusion coefficient $D^{(0)}(\infty)$ for the $N = 104$ and 400 particle systems studied are consistent with the supposition that this quantity is finite in the large system limit, but they are probably also not inconsistent with a slow (logarithmic?) divergence with increasing system size.[8] We should also mention, however that de Schepper and Ernst[27] have found that for two-dimensional systems the true asymptotic time behavior may not be the t^{-1} behavior indicated in Eq. (58), but rather $\rho_D^{(0)}(t) \sim t^{-1}(\ln t)^{-1/2}$, in agreement with the "self-consistent" result of Wainwright, Alder, and

---

[8] Our[15] extension of the mode coupling (or hydrodynamic) theory of Ernst et al.[20] to finite periodic systems indicates that finite system effects will damp the long-time tail given by Eq. (58) so that $D^{(0)}(\infty)$ will be finite for finite two-dimensional systems, but that it will diverge with increasing N. It is possible, however, that the assumptions underlying this hydrodynamic theory are inappropriate for long-ranged interactions.

Gass.[28] There are kinetic theory reasons[27] for believing that the t^{-1} behavior may in fact be dominant at the intermediate times accessible to the computer experiments. The difference between the two behaviors would be difficult to distinguish in any case, owing to the limited precision and time scales of the numerical studies. In either case, the self-diffusion coefficient is divergent.

Somewhat in the spirit of Professor Cohen's original suggestion are the *steady state* self-diffusion molecular dynamics calculations which we carried out with Dr. Brad Holian,[15,16] using a procedure similar to the nonequilibrium molecular dynamics methods of Ashurst and Hoover.[29] These calculations were done for both hard disks and hard spheres, over a range of system sizes, but at a single density. The values of $D^{(0)}$, estimated from the ratio of the diffusion current to the slope of the observed linear profile of the species number density, were of course finite for the finite systems studied for both $d = 2$ and $d = 3$, and were in reasonable agreement with Eq. (25) extrapolated to $t = \infty$ with use of the observed finite system values of the velocity autocorrelation function. They appear to be consistent with the hypothesis of approach to a constant value with increasing system size for the three-dimensional case, and with a slow (logarithmic?) divergence with system size in two dimensions. Lebowitz and Spohn[30] have recently been able to show theoretically, under certain assumptions, that this model should indeed approach at long times a steady state with a linear density profile, and with a diffusion constant given by the time integral of the velocity autocorrelation function.

Lorentz Systems

Lorentz gases, in which independent point particles diffuse within a system of infinitely massive scatterers, provide an interesting simplification of the diffusion process in fluids. Here the study of the motion of a single particle is all that is necessary, because of the absence of interactions among the independently moving point particles. The cases in which the scatterers are hard disks or spheres, either overlapping or nonoverlapping, have been studied both theoretically[31] and by molecular dynamics.[32-36] The theory[31] again finds at low scattering densities a power-law decay of the velocity autocorrelation function, as given by Eq. (58), but with $p = 1 + d/2$, so that $D^{(0)}(\infty)$ is convergent for both $d = 2$ and $d = 3$. The early molecular dynamics investigations[32-35] confirmed the predicted power-law decay at low densities, but found values of the coefficient $\alpha_D^{(0)}$ about three times larger than the theoretical value. Recently, however, Alley[36] found good agreement with the latter by extrapolating the observed density-dependent values from three very low density calculations to

zero density. There appears to be as yet no theoretical explanation for the very strong density dependence of the coefficient, or for the observed density dependence of the power-law exponent.

Bunimovich and Sinai[37] have recently proved some rigorous theorems for finite two-dimensional Lorentz systems under periodic boundary conditions, one of which relates to the asymptotic behavior of the velocity autocorrelation function. If collision events between the moving particle and the scatterers are enumerated by $n = 0, 1, 2, \ldots$, and if $\mathbf{v}_n$ denotes the postcollision velocity, then they show that for large enough n

$$\langle \mathbf{v}_n \cdot \mathbf{v}_0 \rangle \leqslant v_0^2 \exp(-n^\gamma) \tag{59}$$

with $0 < \gamma \leqslant 1$. The average is over the initial phase of the moving particle, for any fixed periodic scattering configuration satisfying certain assumptions. There are apparently technical difficulties in translating the above result from its statement in terms of the collision index n into a corresponding statement in terms of the usual *time* correlation function. Also, it is quite possible (but not proved) that the above result applies only for such large n that the root-mean-square displacement is large compared to the fixed period of the scattering configuration. For these reasons, there is no necessary inconsistency with the power-law decay found by the above-mentioned kinetic theory and molecular dynamics investigations.

Beyond Navier–Stokes

Soon after the discovery by Alder and Wainwright[13] of the long-time tails of the time correlation functions corresponding to the Navier–Stokes (including therein the Fick's law) transport coefficients, Dorfman and Cohen[19] and Ernst, Hauge, and van Leeuwen[20] noted that the theoretical arguments which accounted for the behavior of those correlation functions would also predict that the temporally local Burnett and super-Burnett, etc., coefficients such as $D^{(2)}(t)$ in Eq. (23) would diverge with increasing t in *both* two and three dimensions. The detailed kinetic theory and mode-coupling derivations of these conclusions for simple fluid systems have been given by de Schepper *et al.*,[38,39] correcting earlier similar results obtained by others.[40,41] We[15,16] have reported molecular dynamics calculations of $D^{(2)}(t)$ for hard disks (agreeing with similar results obtained by Alder[42]) and for hard spheres which, within their rather large error limits, tend to support these predictions. In addition Alley and Alder[34–36] have carried out molecular dynamics calculations of $D^{(2)}(t)$ for Lorentz disks with similar conclusions. They[11,36] were apparently the first to suggest that the temporally *nonlocal* higher-order transport coefficients $\mathcal{D}^{(2n)}(t)$ appearing in Eqs. (39) and (40) might be convergent in the

long-time limit even if $D^{(2)}(t)$, etc., were not. [In fact, they conjectured that this might be so for all systems for which $D^{(0)}(t)$ is convergent.] They presented molecular dynamics evidence that this is indeed true for the Lorentz hard-disk system. Going one step further, they also argued that an additional transformation to a "vortex-moving reference frame" would lead to a convergent super-Burnett coefficient for three-dimensional fluid systems. This conjecture is in conflict[43] with the theoretical results of de Schepper et al.,[38] but the convergence of $\mathcal{D}^{(2)}(t)$ for the Lorentz disk system has been confirmed from kinetic theory arguments by Ernst and van Beijeren.[43] [9] The published molecular dynamics data for the super-Burnett coefficient for hard spheres do not appear to distinguish unambiguously whether the Alley and Alder modified $\mathcal{D}^{(2)}(t)$ is convergent or not.

Asymptotic Behavior of $G_s(\mathbf{r}, t)$

Our discussion has confirmed the familiar fact that the van Hove self-correlation function $G_s(\mathbf{r}, t)$ is the fundamental quantity for the self-diffusion process. For a classical isotropic diffusion process with a constant diffusion coefficient D, this function is the Gaussian

$$G_{cl}(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(\frac{-r^2}{4Dt} \right) \tag{60}$$

One important question, then, is whether $G_s(\mathbf{r}, t)$ for any particular model of interest will in some sense approach this form in the long-time limit. We note that this question is well posed only for systems for which the limit $D = D^{(0)}(\infty)$ exists. For the three-dimensional fluid, where this condition is met, de Schepper and Ernst[39] have used mode-coupling theory to answer the question in the affirmative, obtaining a series of the form

$$G_s(\mathbf{r}, t) = G_{cl}(\mathbf{r}, t)\left[1 - b_1(\rho)t^{-1/2} - b_2(\rho)t^{-3/4} - \cdots + O(t^{-1}) \right] \tag{61}$$

in which the coefficients depend upon $\mathbf{r}$ and t only through the dimensionless combination $\rho = r/(Dt)^{1/2}$. Our molecular dynamics results[15] are consistent with this conclusion.

Alley and Alder[34] have presented molecular dynamics evidence that $G_s(\mathbf{r}, t)$ approaches Gaussian form at long times for the Lorentz hard-disk system, for which $D^{(0)}(\infty)$ also exists. Bunimovich and Sinai[37] have shown rigorously that this should indeed be the case.

For the hard-disk fluid, for which $D^{(0)}(t)$ is divergent, one needs to rephrase the question slightly, to ask whether $G_s(\mathbf{r}, t)$ might approach at

---

[9] This last-mentioned paper also discusses the long-time behavior of these quantities for various one-dimensional systems.

long times the related Gaussian

$$G_{cl}(\mathbf{r}, t) = \frac{1}{\pi \langle \Delta r^2(t) \rangle} \exp\left[\frac{-r^2}{\langle \Delta r^2(t) \rangle} \right] \tag{62}$$

We[15] and Alley and Alder[34] have published molecular dynamics results for hard disks which suggest that the trend of $G_s(\mathbf{r}, t)$ at long times is away from the Gaussian form.

ACKNOWLEDGMENTS

APPENDIX: TRANSPORT IN FINITE PERIODIC SYSTEMS

One often sees statements to the effect that transport coefficients, as given by the Green–Kubo formulas, are necessarily zero in a finite system, and hence that passage to the thermodynamic limit must be done first, followed by taking the long-time limit, in order to obtain meaningful results. One basis for these statements is the Einstein formula for the self-diffusion coefficient,

$$D^{(0)} = \lim_{t \to \infty} \left[\Delta x_1^2(t)/2t \right]$$

which is clearly zero for a finite system with rigid boundaries, since $\Delta x_1(t)$ is bounded. What we wish to point out is that these assertions are not necessarily correct for the periodic boundary conditions usually employed in computer experiments. Our remarks are essentially an elaboration of a discussion by Lebowitz.[44]

In actuality, periodic boundary conditions can be applied in two related, but different, ways. One possibility is the toroidal interpretation, in which the particles are considered to move on the surface of a torus, with a geodesic metric which is equivalent to the familiar "minimum image distance" convention. This is the interpretation frequently described by saying that a particle which leaves the system through one face of the volume V (usually a rectangular parallelepiped) simultaneously reenters through the opposite face. When this is done $\Delta x_1(t)$ is again bounded (by half the period of the system), and $D^{(0)}$ as given by the Einstein formula will again vanish in the long-time limit. Another disadvantage of this

procedure is that $v_{1x}(t) = d\Delta x_1(t)/dt$ is no longer a (piecewise, for hard cores) continuous function of t, there being δ-function contributions at those times when $|\Delta x_1(t)|$ is equal to a half-period. This leads to ambiguities in the calculation of the transport coefficients.

An alternative interpretation of periodic boundary conditions is the "infinite checkerboard" or "crystallographic" version, in which d-dimensional space is filled by periodic replication of the fundamental cell of volume V containing its N particles and their velocity vectors. Each particle is considered to be labeled with both its particle index i (running from 1 to N) and a cell index ν identifying the cell in which it was located at the initial time. The particle coordinates, e.g., the x coordinate $x_{10}(t)$ of particle $i = 1$, $\nu = 0$ and the corresponding displacement $\Delta x_{10}(t)$ are then continuous functions of t, and can take on any values in the infinite interval. The previous simple argument for a vanishing diffusion constant no longer applies. Of course, it does not follow that it is in fact nonzero or even finite. As far as we are aware, the question is unsettled, in general. The results of Bunimovich and Sinai[37] appear to show that the diffusion coefficient for a finite, periodic, hard-disk Lorentz gas is nonzero and finite under the checkerboard interpretation. Under this "checkerboard" interpretation $v_{10x}(t) = d\Delta x_{10}(t)/dt$ is a (possibly piecewise) continuous function of t, without any extraneous δ functions. Thus the usual equivalences between relations such as Eqs. (22) and (25) hold. We have shown elsewhere[16] how this viewpoint leads to a novel expression for the equation of state. It is also the most natural way in which to evaluate the time correlation functions associated with other transport coefficients, such as the shear viscosity.[45]

REFERENCES

1. W. W. Wood, in *The Boltzmann Equation, Theory and Applications*, E. G. D. Cohen and W. Thirring, eds. (Acta Physica Austriaca, Suppl. X), (Springer, Berlin, 1973), p. 451.
2. J. L. Lebowitz and H. Spohn, *J. Stat. Phys.* **19**:633 (1978).
3. J. R. Dorfman, in *Fundamental Problems in Statistical Mechanics III*, E. G. D. Cohen, ed. (North-Holland, Amsterdam, 1975), p. 277.
4. B. J. Berne, in *Physical Chemistry, An Advanced Treatise*, Vol. VIII-B *Liquid State*, D. Henderson, ed. (Academic Press, New York, 1971), p. 540.
5. J. A. McLennan, *Phys. Rev. A* **8**:1479 (1973).
6. M. H. Ernst, B. Cichocki, J. R. Dorfman, J. Sharma, and H. van Beijeren, *J. Stat. Phys.* **18**:237 (1978).
7. J. W. Dufty, private communication.
8. N. G. van Kampen, *Phys. Norwegica* **5**:10 (1971).
9. H. J. Raveche and J. E. Mayer, *J. Chem. Phys.* **52**:3990 (1970).
10. L. van Hove, *Phys. Rev.* **95**:249 (1954).
11. W. E. Alley and B. J. Alder, *Phys. Rev. Lett.* **43**:653 (1979).
12. T. L. Hill, *Statistical Mechanics*, (McGraw-Hill, New York, 1956), p. 233.
13. B. J. Alder and T. E. Wainwright, *Phys. Rev. Lett.* **18**:968 (1967); *J. Phys. Soc. Jpn.* **26** Suppl.:267 (1969), (Proc. Int. Conf. Stat. Mech., Kyoto, 1968); *Phys. Rev. A* **1**:18 (1970).

14. G. Subramanian, D. Levitt, and H. T. Davis, *J. Chem. Phys.* **60**:2 (1974); G. Subramanian and H. T. Davis, *Phys. Rev. A* **11**:1430 (1975).
15. W. W. Wood, in *Fundamental Problems in Statistical Mechanics III*, E. G. D. Cohen, ed. (North-Holland, Amsterdam, 1975), p. 331.
16. J. J. Erpenbeck and W. W. Wood, in *Statistical Mechanics, Part B: Time-Dependent Processes*, B. J. Berne, ed. (Vol. 6 of *Modern Theoretical Chemistry*, W. H. Miller, H. F. Schaefer III, B. J. Berne, and G. A. Segal, eds.), (Plenum, New York, 1977), p. 1.
17. D. Levesque and W. T. Ashurst, *Phys. Rev. Lett.* **33**:277 (1974).
18. S. Toxvaerd, *Phys. Rev. Lett.* **43**:529 (1979).
19. J. R. Dorfman and E. G. D. Cohen, *Phys. Rev. Lett.* **25**:1257 (1970); *Phys. Rev. A* **6**:776 (1972); **12**:292 (1975).
20. M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, *Phys. Rev. Lett.* **25**:1254 (1970); *Phys. Lett.* **34A**:419 (1971); *Phys. Rev. A* **4**:2055 (1971); *J. Stat. Phys.* **15**:7, 23 (1976).
21. Y. Pomeau and P. Resibois, *Phys. Rev.* **19**:63 (1975).
22. J. R. Dorfman and H. van Beijeren, in *Statistical Mechanics, Part B: Time-Dependent Processes*, B. J. Berne, ed. (Plenum, New York, 1977), p. 65.
23. S. Yip, *Ann. Rev. Phys. Chem.* **30**:547 (1979).
24. H. van Beijeren and M. H. Ernst, *J. Stat. Phys.* **21**:125 (1979).
25. J. R. Dorfman, *Studies in Statistical Mechanics*, Vol. IX *Perspectives in Statistical Physics* (North-Holland, Amsterdam, 1981).
26. J. P. Hansen, D. Levesque, and J. J. Weis, *Phys. Rev. Lett.* **43**:979 (1979).
27. I. M. de Schepper and M. H. Ernst, *Physica* **87A**:35 (1977).
28. T. E. Wainwright, B. J. Alder, and D. M. Gass, *Phys. Rev. A* **4**:233 (1971).
29. W. T. Ashurst and W. G. Hoover, *Phys. Rev. Lett.* **31**:206 (1973); *Phys. Rev. A* **11**:658 (1975).
30. J. L. Lebowitz and H. Spohn, private communication.
31. M. H. Ernst and A. Weyland, *Phys. Lett.* **34A**:39 (1971).
32. C. Bruin, *Phys. Rev. Lett.* **29**:1670 (1972); *Physica* **72**:261 (1974).
33. J. C. Lewis and J. A. Tjon, *Phys. Lett.* **66A**:349 (1978).
34. B. J. Alder and W. E. Alley, *J. Stat. Phys.* **19**:341 (1978).
35. B. J. Alder, in *Lecture Notes in Physics*, Vol. 84, L. Garrido, P. Seglar, and P. J. Shepherd, eds. (Springer, Berlin, 1978), p. 169.
36. W. E. Alley, thesis Studies in Molecular Dynamics of the Friction Coefficient and the Lorentz Gas, University of California, Lawrence Livermore National Laboratory, Livermore, California, 1979.
37. L. A. Bunimovich and Y. G. Sinai, *Commun. Math. Phys.* **78**:479 (1981); Y. G. Sinai, *Ann. N.Y. Acad. Sci., Nonlinear Dynamics* (1980), p. 143.
38. I. M. de Schepper, H. van Beijeren, and M. H. Ernst, *Physica* **75**:1 (1974); I. M. de Schepper, thesis Generalized Hydrodynamics of the Diffusion Process, Nijmegen (1974); I. M. de Schepper and M. H. Ernst, *Physica* **93A**:611 (1978).
39. I. M. de Schepper and M. H. Ernst, *Physica* **98A**:189 (1979).
40. T. Keyes and I. Oppenheim, *Physica* **70**:100 (1973); H. H-H. Yuan and I. Oppenheim, *Ibid.* **90A**:1, 21, 561 (1978).
41. J. W. Dufty and J. A. McLennan, *Phys. Rev. A* **9**:1266 (1974).
42. B. J. Alder, private communication.
43. M. H. Ernst and H. van Beijeren, *J. Stat. Phys.*, **26**:1 (1981).
44. J. L. Lebowitz, in *Statistical Mechanics: New Concepts, New Problems, New Applications*, S. A. Rice, K. F. Freed, and J. C. Light, eds. (University of Chicago Press, Chicago, 1972), p. 41.
45. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.*, **24**:455 (1981).