Kinetic Equations and Density Expansions: Exactly Solvable One-Dimensional System*

J. L. LEBOWITZ

Belfer Graduate School of Science, Yeshiva University, New York, New York
and
Courant Institute of Mathematical Sciences, New York University, New York, New York

AND

J. K. PERCUS

Courant Institute of Mathematical Sciences, New York University, New York, New York

(Received 26 August 1966)

We have made a detailed study of the time evolution of the distribution function $f(q,v,t)$ of a labeled (test) particle in a one-dimensional system of hard rods of diameter a. The system has a density ρ and is in equilibrium at $t=0$. (Some properties of this system were studied earlier by Jepsen.) When the distribution function f at $t=0$ corresponds to a delta function in position and velocity, then $f(q,v,t)$ is essentially the time-displaced self-distribution function f_s. This function f_s (which can be found in an explicit closed form) and all of the system properties which can be derived from it depend on ρ and a only through the combination $n=\rho/(1-\rho a)$. In particular, the diffusion constant D is given by $D^{-1}=\lim_{s\to 0}[\bar{\psi}(s)]^{-1}=(2\pi\beta m)^{1/2}n$, where $\bar{\psi}(s)$ is the Laplace transform of the velocity autocorrelation function $\psi(t)=\langle v(t)v\rangle$. An expansion of $[\bar{\psi}(s)]^{-1}$ in powers of n, on the other hand, has the form $\sum B_l n^l/s^{l-1}$, leading to divergence of the density coefficients for $l\geq 2$ when $s\to 0$. This is similar to the divergences found in higher dimensional systems. Similar results are found as well in the expansion of the collision operator describing the time evolution of $f(q,v,t)$. The lowest-order term in the expansion is the ordinary (linear) Boltzmann equation, while higher terms are $O(\rho^l t^{l-1})$. Thus any attempt to write a Bogoliubov, Choh-Uhlenbeck–type Markoffian kinetic equation as a power series in the density leads to divergence in the terms beyond the Boltzmann equation. A Markoffian collision operator can, however, be constructed, without using a density expansion, which, e.g., describes the stationary distribution of a charged test particle in the system in the presence of a constant electric field. The distribution of the test particle in the presence of an oscillating external field is also found. Finally, the short- and long-time behavior of the self-distribution is examined.

1. INTRODUCTION

THE nonequilibrium properties of a macroscopic system "close" to equilibrium, such as linear transport coefficients, may be determined from the time-displaced distribution functions[1] (t.d.f.) (giving the probability of finding particles in specified states at two different times) in a manner similar to that in which the equilibrium properties are determined from the equilibrium distribution functions[2] (e.d.f.). Furthermore, some time-displaced distribution functions may be obtained "directly" from neutron-scattering experiments and from molecular-dynamic computations.[3] This, combined with the absence of any partition-function formalism for nonequilibrium systems, makes these functions of central importance in the study of non-

equilibrium processes. Now, while the prescriptions for determining the t.d.f. are as precise as those for the e.d.f. (see Appendix A), their theoretical analysis is far more complex. There are no virial expansions or approximate theories for the t.d.f. comparable[4] to the virial expansions and approximate integral equations which have proven useful for the e.d.f. The questions raised recently[5,6] concerning (a) the divergencies in time of the coefficients in the density expansion of various kinetic equations and (b) the nonanalyticity in the density ρ of transport coefficients are related directly to the properties of the t.d.f. and indicate their possible complexities.

In order to understand more fully the nature of these divergences in the virial expansions and to develop a feeling for how an approximate theory of the t.d.f. might go, we have made an extensive study of the one solvable fluid model.[7] This is a classical system of one-dimen-

[1] L. Van Hove, Phys. Rev. 95, 249 (1954). Formal definitions for classical systems, the only ones we are concerned with here, are given in Appendix A.

[2] M. S. Green, J. Chem. Phys. 22, 398 (1954); R. Kubo, J. Phys. Soc. Japan 12, 570 (1957); R. Zwanzig, Ann. Rev. Phys. Chem. 16, 67 (1965).

[3] A. Rahman, Phys. Rev. 136, A405 (1964). This paper also contains some interesting approximations for some t.d.f. L. Verlet (to be published).

[4] For some approximate theories, see G. H. Vineyard, Phys. Rev. 110, 999 (1958); J. M. J. van Leeuwen and S. Yip, ibid. 139, A1138 (1965); P. G. de Gennes, Physica 25, 825 (1959); K. S. Singwi, Phys. Rev. 136, A969 (1964); H. Mori, Progr. Theoret. Phys. (Kyoto) 34, 399 (1965).

[5] J. R. Dorfman and E. G. D. Cohen, Phys. Letters 16, 124 (1965); J. Weinstock, Phys. Rev. 140, A460 (1965); R. Goldman and E. A. Freeman, Bull. Am. Phys. Soc. 11, 531 (1965); J. V. Sengers, Phys. Rev. Letters 15, 515 (1965); K. Kawasaki and I. Oppenheim, Phys. Rev. 139, A1763 (1965).

[6] J. M. J. van Leeuwen and A. Weyland, Phys. Letters 19, 562 (1965). This work is most closely related to ours as it treats the diffusion of a single particle moving in a random array of fixed spheres; see, however, Appendix C.

[7] The exact t.d.f. for a harmonic crystal are given in Ref. 1.

sional hard rods of diameter a. A beautiful formulation of this problem for the case where $a=0$, i.e., impenetrable points in one dimension, was given by Jepsen,[8] who also computed explicitly some properties of this system. A more general formulation, especially applicable to systems with finite diameters, is given in Appendix B. For many purposes, however, adding a finite diameter does not introduce any new complications; it merely requires the replacement in certain expressions of the actual volume per particle ρ^{-1} by the reduced volume $\rho^{-1}-a$, i.e., $\rho \rightarrow \rho/(1-\rho a)\equiv n$. (We are always speaking here of the limit of an infinite system with fixed ρ.)

This system of hard spheres is special, or pathological, in that its whole dynamics consists of pairs of neighboring particles interchanging velocities at each collision. Hence the fraction of particles at a given velocity is constant in time. Furthermore when $a=0$ all properties of the system which are independent of particle labeling, i.e., functions which are symmetric in all particle coordinates and velocities, are identical to those of an ideal gas where the particles pass each other without interactions. It is only the distributions of specified (labeled) particles which exhibit normal kinetic behavior, i.e., diffusion and approach to equilibrium. This is true in particular (see Appendix B) of the conditional self-distribution function $f_s(q-q', v, t/v')$ which will be our primary concern here. $f_s(q-q', v, t/v')$ gives the probability density for a particle, in an equilibrium system, to be at position q with velocity v at time t when this particle was known to be at q' with velocity v' at $t=0$. The behavior of f_s is identical to that of a single impenetrable particle moving in an ideal gas of particles with the same mass and density n (a special case of Rayleigh's problem done exactly).

Integrating $f_s(q-q', v, t/v')$ over q and averaging over q' (the latter being unnecessary for the uniform system considered here), we obtain the conditional velocity distribution function

$$h_s(v,t/v') = \int f_s(q,v,t/v')dq. \qquad (1.1)$$

Multiplying $h_s(v,t/v')$ by $h_0(v')$, the equilibrium velocity distribution function[9]

$$h_0(v) = (2\pi/\beta m)^{-1/2} \exp[-\beta mv^2/2] \qquad (1.2)$$

yields the time-displaced self-velocity distribution function. This may be used to compute the velocity autocorrelation function

$$\psi(t) = \langle v(t)v \rangle \equiv \int vh_s(v,t/v')h_0(v')v'dvdv' \qquad (1.3)$$

which may be obtained from Jepsen's result by the

transformation $\rho \rightarrow \rho/(1-\rho a)\equiv n$. The self-diffusion coefficient D is then found immediately to be[8]

$$D= \int_0^\infty \psi(t)dt = \lim_{s\to 0} \tilde{\psi}(s)$$

$$= \frac{1}{2}\frac{(1-\rho a)}{\rho}\langle |v| \rangle = \frac{(1-\rho a)}{\rho(2\pi\beta m)^{1/2}}, \qquad (1.4)$$

where $\tilde{\psi}(s)$ is the Laplace transform of $\psi(t)$, which decays asymptotically as t^{-3}. D may also be obtained from the conditional positional distribution function

$$n_s(q,t)\rightarrow(4\pi Dt)^{-1/2}\exp[-q^2/4Dt], \quad \text{as} \quad t\rightarrow\infty.$$

It is seen from (1.4) that, unlike the situation in two and three dimensions,[5,6] D^{-1} (or ρD) is here an analytic function of ρ. This is so despite the fact, shown explicitly in Sec. 3, that an expansion of $\tilde{\psi}^{-1}(s,\rho)$ in powers of ρ has the form

$$\tilde{\psi}^{-1}(s,\rho)=\beta ms\left\{1+\sum_{l=1}^{\infty} B_l\left[\frac{\rho/s}{(1-\rho a)(\beta m)^{1/2}}\right]^l\right\} \qquad (1.5)$$

with the B_l pure numbers. It is seen from (1.5) that the coefficients of ρ^l for $l\geq 2$ are even more singular here, as $s\rightarrow 0$, than they are in two or three dimensions (where the singularity is logarithmic in s). This shows that small s (or large t) divergences of the kinetic virial coefficients do not necessarily lead to a nonanalyticity of the transport parameters.

A similar, related, result is found when we consider the kinetic equation describing the time evolution of the distribution $f(q,v,t)$ of a test particle in the system, i.e., a test particle with the same properties as the other particles of the system,

$$f(q,v,t) = \int f_s(q-q', v, t/v')f(q',v',0)dq'dv', \qquad (1.6)$$

where $f(q,v,0)$ is arbitrary, and the rest of the system is in equilibrium at $t=0$ with respect to the distribution of the test particle.

The time evolution of $f(q,v,t)$ will satisfy a generalized linear kinetic equation of the form[6,10]

$$\frac{\partial f(q,v,t)}{\partial t}+v\frac{\partial f}{\partial q}\equiv \mathbf{B}f\equiv \int_0^t dt' \int dq' \int dc$$

$$\times B(q-q', t-t'; v, c)f(q',c,t')dc. \qquad (1.7)$$

The collision operator $\mathbf{B}$, which again depends on n, may be found "explicitly" for this model. Equation (1.7) will lead to the velocity part of $f(q,v,t)$ becoming Maxwellian as $t\rightarrow\infty$ [the coordinate part tending to a uniform value which may or may not be zero depending on the normalization of $f(q,v,0)$]. Also $\mathbf{B}$ will decay, albeit nonexponentially, as $t\rightarrow\infty$. An expansion of B in powers of

[8] D. W. Jepsen, J. Math. Phys. **6**, 405 (1965). [For some earlier work on this system see also H. L. Frisch, Phys. Rev. **104**, 1 (1956).]

[9] For this gas *any* velocity distribution function is stationary and all our general results apply to an arbitrary $h_0(v)$. For explicit results with a non-Maxwellian $h_0(v)$ see Sec. 7.

[10] J. L. Lebowitz and P. Resibois, Phys. Rev. **139**, A1101 (1965) [see their Eq. (2.26)].

n will however lead to divergences. Thus considering for simplicity only the velocity part of B,

$$B(t-t';v,c)=\int dqB(q-q',t-t';v,c),\quad(1.8)$$

which is all that enters when $f(q,v,0)$ is spatially uniform, and expanding it in powers of n yields

$$B(t-t';v,c,n)=\sum_{l=1}^{\infty}n^{l}B_{l}(t-t';v,c)$$
$$=n\delta(t-t')B_{1}'(v,c)+n^{2}B_{2}(v,c)+\cdots.\quad(1.9)$$

The first term corresponds to the linear Boltzmann equation while the second term is independent of $t-t'$ [the term of order n^{l} will be proportioanl to $(t-t')^{l-2}$]. The kinetic equation will thus not be Markoffian beyond the lowest-order term in n and any attempt to obtain an approximate Markoffian equation valid on some long time scale in the manner of Bogoliubov[11] will lead to divergences similar to (but stronger than) those found in higher dimensions.[5,6] More precisely, if we try to put our kinetic equation (using the spatially homogeneous case for simplicity) in the Bogoliubov, Choh-Uhlenbeck[12] form appropriate here,[13] i.e., we have the collision term depending only on the value of f at time t,

$$\frac{\partial f(v,t)}{\partial t}\simeq\sum_{l=1}^{\infty}n^{l}\int dc\int_{0}^{t}B_{l}(t';v,c)dtf(c,t)$$

$$=\sum_{l=1}^{\infty}n^{l}\int B_{l}'(t;v,c)f(c,t)dc,\quad(1.10)$$

then

$$\lim_{t\to\infty}B_{l}'(t;v,c)=0(t^{l-1}).\quad(1.11)$$

We may, on the other hand, use the above procedure without making any expansion in the density, writing

$$\frac{\partial f(v,t)}{\partial t}\simeq\int U(v,c)f(c,t)dc,\quad(1.12)$$

where

$$U(v,c)=\lim_{t\to\infty}\int_{0}^{t}B(t';v,c)dt'.\quad(1.13)$$

The operator U is linear in n, different from B_{1}', and (1.12) leads to $f(v,t)$ approaching $h_0(v)$ "monotonically" as $t\to\infty$. Equation (1.12) yields the correct diffusion constant D while the Boltzmann equation does not (see Ref. 14).

[11] N. N. Bogoliubov, *Studies in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 5.

[12] S. T. Choh and G. E. Uhlenbeck, work done under U. S. Navy Contract No. Nonr-1224 (15), University of Michigan, 1958 (unpublished).

[13] The form appropriate here would be obtained by starting with a mixture of particles of species α and β with densities ρ_α and $\rho_\beta=\rho$ (both species being hard rods of diameter a). The kinetic equation for the one-particle distribution function of species α in the limit $\rho_\alpha\to0$ when species β is initially in equilibrium would then coincide with (1.7).

[14] It is to be noted that D and other properties of this system "coincide" with those given by the Enskog theory of hard spheres.

The failure of the Bogoliubov method for this problem is no surprise since its underlying idea, the existence of two time scales, is not valid here. The only time scale available here is the mean free time between collisions $\tau_m\sim(\rho\langle|v|\rangle)^{-1}$. The shorter time scale corresponding to the duration of a collision, $\tau_c\sim a/\langle|v|\rangle$, never enters here since a and ρ only appear in the combination n, i.e., there is only one length, n^{-1}, in our problem. It is therefore possible that in two and three dimensions the operator corresponding to U in (1.13) will give a valid description of the evolution of $f(v,t)$ for $t\gg\tau_c$.

2. THE SELF-DISTRIBUTION

The self-distribution $f_s(q,v,t/v')$ may be obtained either by Jepsen's method or from our general method, given in Appendix B.

One finds that for $a=0$ (when $a\neq0$, ρ is replaced by n everywhere)

$$f_{s}(q,v,t/v')=A(v,t)\delta(v-v')\delta(q-vt)+\rho h_{0}(v)\frac{1}{2\pi}$$
$$\times\int_{0}^{2\pi}F(t\rho,\theta,q/t)\exp(i\theta[\epsilon(q-v't)-\epsilon(vt-q)])d\theta$$
$$=h_{0}(v)L(q,t;v,v').\quad(2.1)$$

Here $\epsilon(z)$ is a step function

$$\epsilon(z)=0,\quad z<0$$
$$=1,\quad z>0,\quad(2.2)$$

$$F(t\rho,\theta,v)=\exp\{-t\rho[(1-\cos\theta)\mu(v)-iv\sin\theta]\},\quad(2.3)$$

$$\mu(v)=\int|v-w|h_{0}(w)dw,\quad(2.4)$$

and

$$A(v,t)=\frac{1}{2\pi}\int_{0}^{2\pi}F(t\rho,\theta,v)d\theta$$
$$=e^{-t\rho\mu(v)}I_{0}(t\rho[\mu^{2}(v)-v^{2}]^{1/2}),\quad(2.5)$$

where I_0 is the zeroth-order modified Bessel function of the first kind. The function L is symmetric in v and v' and satisfies the reflection symmetry

$$L(q,t;v,v')=L(-q,t;-v,-v').\quad(2.6)$$

[Note that $F(t\rho,\theta,v)$ and $A(v,t)$ depend on t only through the combination $t\rho$, so that any expansion in ρ will have infinite coefficients as $t\to\infty$.]

The quantity $A(v,t)$, which coincides with $A_{oo}(v,t)$ of Jepsen, is the probability that a particle having velocity v at $t=0$ will also have velocity v at time t, either because it had no collision up to t (this has probability $e^{-t\rho\mu(v)}$) *or*

In that theory D is obtained from its value for a dilute system by replacing the density ρ appearing in the latter by $\rho g(a)$, where $g(a)$ is the value of the equilibrium radial distribution function at contact, which is here equal to $(1-\rho a)^{-1}$. For the one-dimensional system considered here, the diffusion constant obtained from the Boltzmann equation is off by 16% [J. M. J. van Leeuwen and A. Weyland (private communication)].

because its last collision before t was with the neighbor it initially collided with, and the latter had not yet collided with a different particle (giving rise to the factor I_0).

Taking the spatial Fourier and Laplace time (FL) transform of f_s yields [see Appendix B, Eq. (24)]

$$K(k,s; v,c) = \int_0^\infty dt\, e^{-st} \int_{-\infty}^\infty dq\, e^{ikq} f_s(q,v,t/c)$$

$$= \tilde{A}(v, s-ikv)\delta(v-c) + \rho h_0(v) \int_{-\infty}^\infty dw$$

$$\times \{\rho\mu(w) + \epsilon[(v-w)(w-c)](s-ikw)$$

$$+ \rho w[\epsilon(v-w) - \epsilon(w-c)]\}[\tilde{A}(w, s-ikw)]^3$$

$$= h_0(v)\tilde{L}(k,s; v,c), \qquad (2.7)$$

where

$$\tilde{A}(v,s) = [\rho^2 v^2 + 2s\rho\mu(v) + s^2]^{-1/2} \qquad (2.8)$$

is the Laplace transform of $A(v,t)$ and $\tilde{L}(k,s; v,c)$, the FL transform of L, is symmetric in v and c.

The Laplace transform $\tilde{h}(s; v,c)$ of the conditional velocity distribution function (1.1) may be obtained from (2.7) by setting $k=0$:

$$\tilde{h}(s; v,c) = K(0,s; v,c). \qquad (2.9)$$

It is now readily verified that as $s \to 0$,

$$\tilde{h}(s; v,c) = h_0(v)/s + o(s^{-1}) \qquad (2.10)$$

which implies

$$\lim_{t \to \infty} h(v,t/v') = h_0(v'). \qquad (2.11)$$

A more detailed analysis of the asymptotic form of f_s is given in Sec. 7.

3. VELOCITY AUTOCORRELATION FUNCTION

The Laplace transform $\tilde{\psi}(s)$ of the velocity autocorrelation function $\psi(t)$ may be obtained, after some manipulation, from (2.7)–(2.9) in the form

$$\tilde{\psi}(s) = \int_{-\infty}^\infty v^2 h_0(v)\tilde{A}(v,s)dv$$

$$\frac{n}{2}\int_{-\infty}^\infty (\mu(v) - v\mu'(v))^2 s[\tilde{A}(v,s)]^3 dv \qquad (3.1)$$

$$= \int_{-\infty}^\infty v^2 h_0(v)\tilde{A}(v,s)dv$$

$$- 2(m\beta)^{-2}n \int_{-\infty}^\infty s h_0{}^2(v)[\tilde{A}(v,s)]^3 dv \qquad (3.1')$$

for a Maxwellian distribution.

Taking now the limit $s \to 0$ we obtain the diffusion constant D given in (1.5), the first integral giving $2D$ and the second $(-D)$. [In evaluating the second integral in (3.1) in the limit $s \to 0$, $h_0(v)$ and $\mu(v)$ may be set

equal to their values at $v=0$.] D^{-1} thus has the form

$$D^{-1} = \alpha n(\beta m)^{1/2}, \qquad (3.2)$$

where $\alpha = (2\pi)^{1/2}$ is a pure number. The general form D^{-1} could have been deduced without any computation (except for the numerical value of α which could have been also 0 or ∞) since for the case $a=0$ there is no dimensionless constant on which α could depend, and we showed earlier that when $a \neq 0$ we simply replace ρ by n. In higher dimensions (hard disks or hard spheres of diameter a) we will generally have

$$D^{-1} = \rho a^{\nu-1}(\beta m)^{1/2}\xi_\nu(\rho a^\nu), \qquad (3.3)$$

where $\nu = 1, 2, 3$ is the number of space dimensions considered. It has been suggested that $\xi_\nu(\eta)$ contains for $\nu = 2, 3$ a term of the form $\eta^{\nu-1}\ln\eta$. This conclusion is based, since $\xi_\nu(\eta)$ cannot be evaluated exactly, on partial summation of diagrammatic expansions occurring in the generalized transport equation (1.7) for $f(q,v,t)$. When $\tilde{\psi}^{-1}$ is computed from this equation[6] in the form of a density expansion,

$$\tilde{\psi}^{-1}(s,\rho) = \nu\beta ms\left[1 + \sum_{l=0}^\infty b_l(s)(\rho a^\nu)^l\right] \qquad (3.4)$$

(the zeroth-order term corresponding to the unhindered motion of an isolated particle, $\rho = 0$), it is found that $b_l(s)$ diverges as $\ln s$ for $l=\nu$, $\nu = 2, 3$. Partial resummation of this expansion then results in the $\ln\rho$ term in $\xi_\nu(\rho a^\nu)$ mentioned earlier.

Let us examine now the behavior of $\tilde{\psi}^{-1}(s,\rho)$ for our one-dimensional model. From the dimensionality argument and from Eq. (3.1) we have

$$\tilde{\psi}^{-1}(s,\rho) = (\beta ms)\left\{1 + \sum_{l=1}^\infty B_l\left[\frac{\rho/s}{(1-\rho a)(\beta m)^{1/2}}\right]^l\right\} \qquad (3.5)$$

with the B_l pure numbers,

$$B_1 = 4/\sqrt{\pi}, \cdots. \qquad (3.6)$$

As $s \to 0$ the coefficients of all ρ^l, for $l \geq 2$, will diverge as s^{1-l}. These divergences do not however have any effect on the analyticity of $D^{-1}(\rho) = \lim_{s \to 0}\tilde{\psi}^{-1}(s,\rho)$. All the divergences indicate, in this case at least, is that the approach of $\rho\psi(t)$ to its asymptotic form is not uniform in the density. Indeed an inspection of (3.5) shows that the only way for the coefficients in the density expansion of $\tilde{\psi}^{-1}(s,\rho)$ to remain finite as $s \to 0$ is for all the B_l to vanish for $l > 1$. This would correspond to $\psi(t)$ having an exponential decay, Langevin type, $\psi(t) = \langle v^2 \rangle$ $\times \exp[-tB_1\rho/(\beta m)^{1/2}]$. For short times, this form of $\psi(t)$ is exact, ψ being linear in t rather than quadratic,[1,4] because of the discontinuity of the interparticle potential. Indeed, an explicit calculation of $\psi(t)$ shows almost perfect coincidence with the exponential form, deviations occurring for $t \gtrsim 4(\beta m)^{1/2}/B_1\rho$ where the exact $\psi(t)$ becomes negative and very very small (see Fig. 1 and the discussion in Sec. 7).
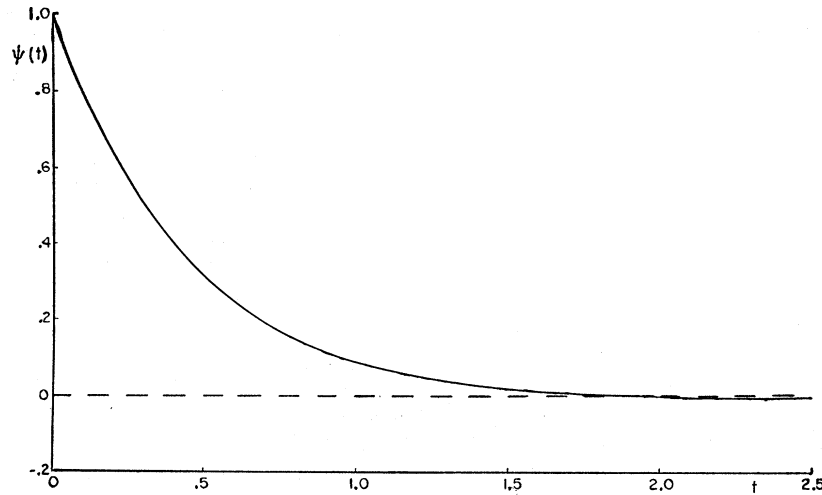
FIG. 1. Short-time behavior of velocity autocorrelation function for one-dimensional hard points at unit density and temperature.

4. KINETIC EQUATION

We now consider the time evolution of the distribution function $f(q,v,t)$ of a test particle, as given by Eq. (1.6). It follows from the symmetry of $L(q,t; v,v') = f_s(q,v,t/v')/h_0(v)$ and from the normalization

$$\int f_s(q,v,t/v')dqdv = 1$$

that whenever $f(q,v,0) = Ch_0(v)$, where C is a constant, then $f(q,v,t) = Ch_0(v)$, independently of t. Thus, the Boltzmann distribution is, as it must be, a stationary state of the stochastic process represented by the transition probability $f_s(q,v,t/c)$. Furthermore, it follows from the results of Sec. 7 that as $t \to \infty$ the velocity part of f becomes Maxwellian and the spatial part tends to uniformity. The Boltzmann distribution is therefore the unique stationary state of this process.

The time evolution may be expressed by means of a collision operator **B**, defined by Eq. (1.7). To obtain an explicit form for this collision operator, we first take the FL transform of Eqs. (1.6) and (1.7), using (2.7):

$$\tilde{f}(k,v,s) = \mathbf{K}f(h,v,0) = \int K(k,s; v,c)f(k,c,0)dc, \quad (4.1)$$

$$(s - ikv)\tilde{f} = f(k,v,0) + \mathfrak{B}\tilde{f}, \quad (4.2)$$

where $\mathbf{K}$ and $\mathfrak{B}$ are operators in velocity space. Comparing (4.1) and (4.2), we have

$$\mathfrak{B} = \mathbf{s} - ik\mathbf{v} - \mathbf{K}^{-1}, \quad (4.3)$$

where $\mathbf{K}^{-1}$ is the operator inverse of $\mathbf{K}$, and $\mathbf{s}$ and $k\mathbf{v}$ are diagonal operators in velocity space. We now rewrite K and $\mathfrak{B}$ in the form

$$K(k,s; v,c) = \tilde{A}(v,s - ikv)[\delta(v - c) + h_0(v)D(k,s; v,c)\tilde{A}(c, s - ikc)], \quad (4.4)$$

$$\mathfrak{B}(k,s; v,c) = [s - ikv - \tilde{A}^{-1}(v, s - ikv)]\delta(v - c) + h_0(v)H(k,s; v,c), \quad (4.5)$$

where D is known explicitly from (2.7). Equation (4.3) then implies the integral equation for H (which is symmetric in the velocity variables)

$$H(k,s; v,c) = D(k,s; v,c) - \int D(k,s; v,v')h_0(v')$$

$$\times \tilde{A}(v', s - ikv')H(k,s; v',c)dv'. \quad (4.6)$$

The kinetic equation describing the time evolution $f(q,v,t)$ may also be obtained more directly (or at least more physically) from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. This gives, for our case, where collisions have the simple effect of interchanging velocities,

$$\frac{\partial f(q,v,t)}{\partial t} + v\frac{\partial f}{\partial q} = \int dv' |v - v'| \{\epsilon(v' - v)f_{(1)}(q,v',q_+,v,t) + \epsilon(v - v')f_{(-1)}(q,v',q_-,v,t)$$

$$- \epsilon(v - v')f_{(1)}(q,v,q_+,v',t) - \epsilon(v' - v)f_{(-1)}(q,v,q_-,v',t)\}. \quad (4.7)$$

Here $f_{(1)}(q,v,q',v',t)$ is the joint probability density of the test particle (at q and v) and its neighbor to the right (at q' and v') and q_+ is the point $q + a$ corresponding to the particles in contact. $f_{(-1)}$ similarly describes the joint distribution of the test particle with its left neighbor.[15] (We take here $t > 0$, and we shall omit the subscript on q from now on.)

---

[15] While we have not seen (or given) an explicit derivation of (4.7), it appears self-evident; see e.g., H. Grad, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. XII, p. 205.

Writing $f_{(1)}(q,v,q,v',t)$ as a linear functional of $f(q,v,t)$

$$f_{(1)}(q,v,q,v',t) = \int_0^t dt' \int dq'dw\phi(q-q',\ t-t';\ v,\ v',\ w)f(q',w,t')$$

$$= \int_0^t dt' \int dq'dw \int dq''\phi(q-q',\ t-t';\ v,\ v',\ w)f_s(q'-q'',w,t'/c)f(q'',c,0)dc \quad (4.8)$$

the Fourier-Laplace transform of ϕ has the form

$$\tilde{\phi}(k,s;\ v,v',w) = \int \tilde{f}_{(1)}(k,s,v,v'/c)\mathbf{K}^{-1}(k,s;\ c,w)dc. \quad (4.9)$$

Here $f_{(1)}(q,v,q',v',t/c)$ is the value of the joint distribution function of the test particle and its right neighbor when the test particle is initially at the origin with velocity c; $\mathbf{K}^{-1}$ is the previously defined *operator* inverse of $\mathbf{K}$. In terms of $\tilde{\phi}$, the collision operator $\mathfrak{B}$ has the form

$$\mathfrak{B}(k,s;\ v,c) = \int dv'|v-v'|\{\epsilon(v'-v)\tilde{\phi}(k,s;\ v',v,c) + \epsilon(v-v')\tilde{\phi}(-k,\ s;\ -v',\ v,\ -c)$$

$$-[\epsilon(v-v')\tilde{\phi}(k,s;\ v,v',c) + \epsilon(v'-v)\tilde{\phi}(-k,\ s;\ -v,\ -v',\ -c)]\} = \mathfrak{B}_+(k,s;\ v,c) - \mathfrak{B}_-(k,s;\ v,c) \quad (4.10)$$

with $\mathfrak{B}_+$ ($\mathfrak{B}_-$) corresponding to collisions which scatter the test particle into (out of) the velocity range $(v,\ v+dv)$. In deriving (4.10) use was made of the reflection invariance of our system.

An explicit calculation of $f_{(1)}(k,s,v,v'/c)$ yields

$$\tilde{f}_{(1)}(k,s,v,v'/c) = \epsilon(v-v')\{\rho h_0(v')K(k,s,v/c) + \rho h_0(v)W(k,s,v',c)\} + \epsilon(v'-v)\{\rho h_0(v)K(k,s,v'/c) + \rho h_0(v')W(k,s,v,c)\},$$

$$(4.11)$$

where the first term in the curly brackets corresponds to having no correlation between the particles entering a collision and

$$W(k,s;\ v,c) = \Gamma(v,\ s-ikv)\tilde{A}(v,\ s-ikv)\delta(v-c) + \rho h_0(v)$$

$$\times \int_{-\infty}^{\infty} dw \bigg\{\epsilon(v-c)\epsilon[(v-w)(w-c)][\rho w - (s-ikw)] + \epsilon(v-w)\epsilon(c-w)[2\Gamma(w,\ s-ikw)-1]\rho[\mu(w)+w]$$

$$+\frac{[\rho\mu(w)+s-ikw]}{\rho[\mu(w)-w]}[\tilde{A}^{-1}(w,\ s-ikw)-\rho\mu(w)+s-ikw]\Gamma(w,\ s-ikw)\bigg\}\tilde{A}^3(w,\ s-ikw). \quad (4.12)$$

Here $\Gamma(s-ikw,\ w)\tilde{A}(w,\ s-ikw)$ is the FL transform of

$$\frac{1}{2\pi}\int_0^{2\pi} e^{-i\theta}F(t\rho,\theta,q/t)d\theta,$$

where F is defined in (2.3),

$$\Gamma(s-ikw,\ w) = [\rho\mu(w)+(s-ikw)-\tilde{A}^{-1}(w,\ s-ikw)]/\rho[\mu(w)-w]. \quad (4.13)$$

It may be readily verified that Γ and W have expansions in ρ (or n) beginning with terms of $0(\rho)$.

Combining (4.11) and (4.9) yields [using (4.3)–(4.6)]

$$\tilde{\phi}(k,s;\ v,v',c) = \epsilon(v-v')\{\rho h_0(v')\delta(v-c) + \rho h_0(v)E(k,s;\ v',c)\} + \epsilon(v'-v)\{\rho h_0(v)\delta(v'-c) + \rho h_0(v')E(k,s;\ v,c)\}, \quad (4.14)$$

with

$$E(k,s;\ v,c) = \frac{W(k,s;\ v,c)}{A(c,\ s-ikc)} - \int W(k,s;\ v,p)h_0(p)H(k,s;\ p,c)dp, \quad (4.15)$$

where H was defined in (4.5)–(4.6). The collision operator may now be written in the form

$$\mathfrak{B}(k,s;\ v,c) = \{\rho h_0(v)|v-c| + \tfrac{1}{2}E(k,s;\ v,c)\rho[\mu(v)-v] + \tfrac{1}{2}E(-k,s;\ -v,\ -c)\rho[\mu(v)+v]\}$$

$$-\bigg\{\rho\mu(v)\delta(v-c) + \rho h_0(v)\bigg[\int_{-\infty}^{v} dv'(v-v')E(k,s;\ v',c) + \int_v^{\infty} (v'-v)E(-k,s;\ -v',\ c)dv'\bigg]\bigg\} = \mathfrak{B}_+ - \mathfrak{B}_-, \quad (4.16)$$

where we have used the relations

$$\tfrac{1}{2}[\mu(v)-v]=\int_{v}^{\infty}(v'-v)h_0(v')dv', \quad \tfrac{1}{2}[\mu(v)+v]=\int_{-\infty}^{v}(v-v')h_0(v')dv'. \tag{4.17}$$

It is interesting to note from (4.16) the form of the singular (delta-function) terms in the collision operators, $\mathfrak{B}_+$ and $\mathfrak{B}_-$, whose combination gives the first term on the right side of (4.5).

$$\mathfrak{B}_+(k,s; v,c)=[\rho\mu(v)+(s-ikv)-\tilde{A}^{-1}(v, s-ikv)]\delta(v-c)+\text{(nonsingular terms)},$$
$$\mathfrak{B}_-(k,s; v,c)=\rho\mu(v)\delta(v-c)+\text{(nonsingular terms)}. \tag{4.18}$$

The existence of the delta function in the B_+ term is a consequence of our system being one dimensional. This gives a finite probability to the test particle regaining its initial velocity after sequences of three collisions, e.g., the particle first collides with its right neighbor, then with its left neighbor, then again with its right neighbor which has not had another collision [see discussion following (2.6)].

5. DENSITY EXPANSION OF THE KINETIC EQUATION

We now expand $\mathfrak{B}(k,s; v,c)$ in a power series in n as was done in (1.9) obtaining

$$\mathfrak{B}(k,s; v,c)=\mathfrak{B}_+(k,s; v,c)-\mathfrak{B}_-(k,s; v,c)=n[h_0(v)\,|v-c|\,]-n[\mu(v)\delta(v-c)]$$
$$+n^2\{\tfrac{1}{2}[(v-c)v-|v-c|\mu(v)]h_0(v)+\tfrac{1}{2}[\mu^2(v)-v^2]\delta(v-c)\}[s-ikv]^{-1}$$
$$-n^2 h_0(v)\left\{\tfrac{1}{2}[(v-c)c+|v-c|\mu(c)][s-ikc]^{-1}+\text{sgn}(v-c)\int_c^v dw h_0(w)\frac{(w-v)(w-c)}{s-ikw}\right\}+O(n^3). \tag{5.1}$$

The generalized kinetic equation (1.7) will then have the form

$$\frac{\partial f(q,v,t)}{\partial t}+v\frac{\partial f}{\partial q}=n\int|v-c|\,[h_0(v)f(q,c,t)-h_0(c)f(q,v,t)]dc$$

$$+\tfrac{1}{2}n^2\int_0^t dt'\int dw\int dc h_0(w)\left\{[\,|v-w|\,|v-c|-v^2]h_0(c)f(q-v(t-t'),v,t')\right.$$

$$+[(v-c)v-|v-c|\,|v-w|]h_0(v)f(q-v(t-t'),c,t')-[(v-c)c+|v-c|\,|c-w|]h_0(v)f(q-c(t-t'),c,t')$$

$$\left.-2\epsilon[(v-w)(w-c)][(w-v)(w-c)]h_0(v)f(q-w(t-t'),c,t')\right\}+O(n^3). \tag{5.2}$$

The first-order term in the expansion is just the ordinary Boltzmann equation with ρ replaced[14] by n.

Integrating (5.2) over q or considering the case where $f(q,v,t)=Ch(v,t)$ we obtain an equation for the time evolution of the velocity distribution function $h(v,t)$ which corresponds to the expansion of B given in (1.9). This yields

$$\frac{\partial h(v,t)}{\partial t}=n\int|v-c|\,[h_0(v)h(c,t)-h_0(c)h(v,t)]dc$$

$$+\tfrac{1}{2}n^2\int_0^t dt'\int dc\int dw h_0(w)\left\{[\,|v-c|[\,|v-c|-|v-w|-|c-w|\,]\right.$$

$$\left.+2(v-w)(w-c)\epsilon[(v-w)(w-c)]]h_0(v)h(c,t')+[-v^2+|v-w|\,|v-c|]h_0(c)h(v,t')\right\}+O(n^3). \tag{5.3}$$

It is readily verified that when $f(q,v,t)\sim h_0(v)$ then each term in the expansion of the collision integral vanishes. It is however not clear to us at present whether the expansion after a finite number of terms, beyond the first, will lead to $f(q,v,t)$ approaching its equilibrium value or will give divergent results. Truncation after the first term leads, of course, to a monotonic approach to equilibrium. This can be seen readily if we

define[16] a quantity $w(q,t)$:

$$w(q,t) = \int f(q,v,t)\ln\left[\frac{f(q,v,t)}{h_0(v)}\right]dv$$

$$= \int f(q,v,t)\ln\phi(q,v,t)dv. \tag{5.4}$$

Then $w(q,t)$ achieves its minimum value when $f \propto h_0(v)$ and we have, using only the first term in the expansion (5.2),

$$\frac{\partial w}{\partial t} + \frac{\partial}{\partial q}\int vf(q,v,t)\ln\phi(q,v,t)dv = -n\int dv\int dc|v-c|f$$

$$\times(q,c,t)h_0(v)\left\{\ln\left[\frac{\phi(q,c,t)}{\phi(q,v,t)}\right] + \frac{\phi(q,v,t)}{\phi(q,c,t)} - 1\right\} \leq 0, \tag{5.5}$$

the equality holding only when $f(q,v,t) \propto h_0(v)$. The second term on the left side of (5.5) represents a flow term, which vanishes when $f(q,v,t)$ is spatially uniform. The term on the right is some kind of entropy production term, $w(q,t)$ becoming proportional to the free-energy density of the test particles when $f \propto h_0(v)$.

As was mentioned in the Introduction, any attempt to obtain a kinetic equation in which $\partial f/\partial t$ depends only on the value of f at time t by replacing t' by t in the $f(t')$ occurring in the density expansion of the kinetic integral will lead to divergences, for large t, in the higher-order terms. These divergences are of the same nature and origin as those occurring in the corresponding problem in two and three dimensions: the persistence in correlations between the velocity of the test particle and the system particle with which it is colliding for times of $O(n^{-1})$.

We can obtain however an "approximate" Markoffian equation for $f(q,v,t)$ by replacing t' by t in $f(q',c,t')$ in (1.7) and letting the limit of the integral there go to infinity. Considering the spatially uniform case $f \propto h$ and taking the Laplace transform we obtain [see (1.12)]

$$s\tilde{h}(v,s) = h(v,0) + \int U(v,c)\tilde{h}(c,s)dc, \tag{5.6}$$

where

$$U(v,c) = \lim_{s\to 0}\lim_{k\to 0}\mathfrak{B}(k,s;v,c)$$

$$= -n|v|\delta(v-c) + h_0(v)\mathfrak{IC}(v,c) \tag{5.7}$$

and

$$\mathfrak{IC}(v,c) = \lim_{s\to 0}\lim_{k\to 0}H(k,s;v,c). \tag{5.8}$$

$U(v,c)$ is the collision operator representing the effect of the "fluid" on the motion of a charged test particle in the steady state (see next section).

[16] J. L. Lebowitz and P. G. Bergmann, Ann. Physik **1**, 7 (1957).

To obtain $\mathfrak{IC}(v,c)$ we take the limit $s \to 0$ in Eq. (4.6), which gives in a fairly straightforward manner

$$\mathfrak{IC}(v,c) = \frac{n|vc|}{\mu(0)}\epsilon(-vc) + \int\frac{|v|}{|v'|}h_0(v')\mathfrak{IC}(v',c)dv'$$

$$- \int\epsilon(-vv')\frac{|v|}{\mu(0)}h_0(v')\mathfrak{IC}(v',c)dv', \tag{5.9}$$

where $\mu(0) = \langle|w|\rangle = (\pi\beta m/2)^{-1/2}$. The solution of (5.9) is found to be

$$\mathfrak{IC}(v,c) = \frac{2n|v||c|}{\mu(0)}\epsilon(-vc) = D^{-1}|v||c|\epsilon(-vc). \tag{5.10}$$

The Markoffian collision operator U will then have the form

$$U(v,c) = D^{-1}|vc|\epsilon(-vc)h_0(v) - n|v|\delta(v-c) \tag{5.11}$$

which is linear in n but is different from the Boltzmann collision operator, which is the lowest-order term in the expansion of $\mathfrak{B}$ given in (5.1). U also has the property of making $w(t)$, defined in (5.4), decrease monotonically until $h(v,t) \to h_0(v)$. The term $n|v|$ in (5.11) which gives the rate at which particles are scattered out of the range dv is the reciprocal of the average time that a particle starting with velocity v will spend with this velocity.

The structure of U is sufficiently simple to permit an explicit solution of (5.6), obtaining

$$\tilde{h}(s,v) = \frac{h(v,0)}{s+n|v|} + \frac{|v|h_0(v)}{D[s+n|v|]}[\eta_-(s)\epsilon(v) + \eta_+(s)\epsilon(-v)]$$

$$= \int\tilde{K}'(s;v,c)h(c,0)dc. \tag{5.12}$$

Here $\tilde{K}'$ is the Laplace transform $h(v,t/c)$ when the distribution develops according to the Markoffian equation (5.6), and

$$\eta_+(s) = \int_0^\infty|v|\tilde{h}(v,s)dv = \int_0^\infty dv\frac{|v|h(v,0)}{s+n|v|}$$

$$+ \frac{\eta_-(s)}{2D}\int_{-\infty}^\infty\frac{v^2h_0(v)}{s+n|v|}dv = N_+(s) + \alpha(s)\eta_-(s), \tag{5.13}$$

$$\eta_-(s) = \int_{-\infty}^0 dv|v|\tilde{h}(v,s) = \int_{-\infty}^0\frac{|v|h(v,0)}{s+n|v|}dv$$

$$+ \frac{\eta_+(s)}{2D}\int_{-\infty}^\infty dv\frac{v^2h_0(v)}{s+n|v|}$$

$$= N_-(s) + \alpha(s)\eta_+(s), \tag{5.14}$$

where

$$\alpha(s) = (2D)^{-1}\int_{-\infty}^\infty dv\frac{v^2h_0(v)}{s+n|v|}. \tag{5.15}$$

This yields

$$\eta_\pm(s) = (N_\pm + \alpha N_\mp)/(1 - \alpha^2). \tag{5.16}$$

The velocity autocorrelation function for the system developing according to the Markoffian operator U may

be obtained from (5.12) by letting $h(v,0) = \delta(v'-v)$. This yields

$$\tilde{\psi}'(s) = 2D\alpha(s)/[1+\alpha(s)], \qquad (5.17)$$

where we have used a prime on $\tilde{\psi}$ to distinguish it from the exact $\tilde{\psi}(s)$ given in (3.1). The diffusion constant obtained in this approximation will be identical to the exact one[14]

$$D' = \lim_{s \to 0} \tilde{\psi}' = D. \qquad (5.18)$$

6. EXTERNAL ELECTRIC FIELD

We consider here the velocity distribution function $h(v,t)$ (the spatial part being uniform), when the test particle (but not the other particles of the system) has a unit charge and there is a spatially uniform external electric field $Ee^{i\omega t}$ acting on the system. To linear terms in E, we write

$$h(v,t) = h_0(v) + Ee^{i\omega t}\Phi(v,t). \qquad (6.1)$$

The Laplace transform of Φ will satisfy the equation [see Eq. (3.4), Ref. 10]

$$\Phi(v,0) + (s+i\omega)\tilde{\Phi}(s,v) - \beta v h_0(v)/s$$
$$= \int \mathfrak{B}(s+i\omega; v, c)\tilde{\Phi}(s,c)dc. \qquad (6.2)$$

The steady-state solution

$$\Phi(v) = \lim_{s \to 0} s\tilde{\Phi}(s,v) \qquad (6.3)$$

has the form

$$\Phi(v) = \int_{-\infty}^{\infty} \tilde{K}(i\omega; v,c)\beta c h_0(c)dc$$

$$= h_0(v)\left\{\beta v \tilde{A}(v,i\omega)\right.$$

$$\left. + \frac{n}{m}\int_{-\infty}^{\infty}[nc - i\omega\,\text{sgn}(v-c)]\tilde{A}^3(c,i\omega)dc\right\}. \qquad (6.4)$$

The mobility will be given by [see Eq. (71), Ref. 8]

$$\sigma(\omega) = \beta\tilde{\psi}(i\omega), \qquad (6.5)$$

whose density expansion was given in (3.5) and whose expansion in ω contains terms of the form $\omega^2 \ln\omega$. In the case of a dc field, $\omega = 0$, the stationary state will satisfy the equation

$$-\beta v h_0(v) = \int U(v,c)\Phi(c)dc,$$

whose solution is

$$\Phi(v) = \frac{1}{2}\frac{\beta h_0(v)v}{n|v|}$$

and $\sigma = \beta D$ as required by the Einstein relation. It should be noted that the steady-state distribution has a discontinuity at $v=0$ and is otherwise proportional to $h_0(v)$, in contrast to the results from the usual relaxation-type equations where $(\rho|v|)^{-1}$ is replaced by an average mean free time τ. Whether this feature remains in higher dimensions is an open question.

7. ASYMPTOTIC DISTRIBUTIONS

We conclude with some qualitative remarks on the form of f_s. At very short times, the interaction of a many-body system is ineffective, so that the self-distribution is that of an ideal gas. According to (A15),

$$f_s(q,v,t/v') \to \delta(q-vt)\delta(v-v'), \quad \text{as} \quad t \to 0. \qquad (7.1)$$

On the other hand, as $t \to \infty$, any memory of initial conditions will be lost, and f_s will thus reduce to an equilibrium one-particle distribution, normalized to unity, i.e.,

$$f_s(q,v,t/v') \to 0, \quad \text{as} \quad t \to \infty. \qquad (7.2)$$

To see how the long-time approach is realized, we observe that as $t \to \infty$

$$A(v,t) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \exp\{-t\rho[(1-\cos\theta)\mu(v) - i(\sin\theta)v]\}d\theta \to \frac{1}{2\pi}\int \exp\{-t\rho[\tfrac{1}{2}\theta^2\mu(v) - i\theta v]\}d\theta,$$

or

$$A(v,t) \to [2\pi t\rho\mu(v)]^{-1/2}\exp\left\{-\frac{t\rho}{2}\frac{v^2}{\mu(v)}\right\}, \qquad (7.3)$$

whereas

$$F(t\rho,\theta,q/t) = \exp\{-\rho[(1-\cos\theta)t\mu(q/t) - iq\sin\theta]\} \to \exp[-\tfrac{1}{2}\rho t\mu(0)\theta^2 - i\rho q\theta],$$

so that

$$\int F(t\rho,\theta,q/t)\exp\{i\theta[\epsilon(q-v't) - \epsilon(vt-q)]\}d\theta \to \left(\frac{2\pi}{\rho t\langle|v|\rangle}\right)^{1/2}\exp\left\{-\tfrac{1}{2}\rho\left(q+\frac{\epsilon}{\rho}\right)^2 \Big/ (t\langle|v|\rangle)\right\}, \qquad (7.4)$$

where $\epsilon = \pm 1$ exists only if q is between $v't$ and vt. Hence, for $\rho q \gg 1$, as $t \to \infty$

$$f_s(q,v,t/v') \to (2\pi\rho t\langle|v|\rangle)^{-1/2}\exp[-(1/2)(\rho/\langle|v|\rangle)(q^2/t)][\delta(v-v')\delta(q-vt) + \rho h_0(v)], \qquad (7.5)$$

representing a singular increasingly unlikely "wave front" for the initial particle to retain or regain its velocity, together with a straight diffusion of the initial one-particle density, with diffusion constant $D=\frac{1}{2}\langle|v|\rangle/\rho$.

It is simpler to recognize qualitative regularities if we restrict attention to the coordinate self-distribution function

$$n_s(q,t)\equiv\iint f_s(q,v,t/v')h_0(v')dvdv'=-A\left(\frac{q}{t},t\right)h_0\left(\frac{q}{t}\right)+\frac{\rho}{2\pi}\int d\theta F(t\rho,\theta,q/t)\left\langle\exp\left[i\left(\frac{\theta}{2}\right)\text{sgn}\left(\frac{q}{t}-v\right)\right]\right\rangle_v^2. \quad (7.6)$$

Since

$$\langle\text{sgn}(w-v)\rangle_v=\mu'(w), \quad h_0(w)=\frac{1}{2}\mu''(w), \quad (7.7)$$

(7.6) may be rewritten as

$$\frac{1}{2}\frac{1}{2\pi}\int F(t\rho,\theta,q/t)\left\{\frac{1}{t}\mu''\left(\frac{q}{t}\right)-\frac{\rho}{1-\cos\theta}\left[(1-\cos\theta)\mu'\left(\frac{q}{t}\right)-i\sin\theta\right]^2\right\}d\theta=-\frac{1}{2\pi}\int\frac{1}{2\rho(1-\cos\theta)}\frac{\partial^2}{\partial q^2}F(t\rho,\theta,q/t)d\theta, \quad (7.8)$$

which yields the convenient relationship

$$\frac{\partial}{\partial t}n_s(q,t)=\frac{1}{2}\frac{\partial^2}{\partial q^2}\left\{\left[\frac{q}{t}\mu-\frac{q}{t}\mu'\frac{q}{t}\right]A\left(\frac{q}{t},t\right)\right\}. \quad (7.9)$$

If we note that the asymptotic $A(q/t,t)$ of (7.3) satisfies the diffusion equation

$$\frac{\partial}{\partial t}A\left(\frac{q}{t},t\right)=\frac{1}{2}\frac{\langle|v|\rangle}{\rho}\frac{\partial^2}{\partial q^2}A\left(\frac{q}{t},t\right), \quad (7.10)$$

we have at once the asymptote

$$n_s(q,t)\rightarrow\left(\frac{\rho}{2\pi\langle|v|\rangle t}\right)^{1/2}\exp\left[-\left(\frac{\rho}{2\langle|v|\rangle}\right)\left(\frac{q^2}{t}\right)\right], \quad (7.11)$$

which indeed could have been found directly from (7.5).

The behavior of n_s over the whole time domain is best observed by examples which utilize non-Maxwellian[9] $h_0(v)$. Two limiting cases are those of a finite-range discrete distribution and a very long-range distribution, with velocity scale c:

I. $h_0(v)=\frac{1}{2}[\delta(v-c)+\delta(v+c)], \quad \mu(v)=\max\{c,|v|\},$

II. $h_0(v)=\frac{1}{2}c^2(c^2+v^2)^{-3/2}, \quad \mu(v)=(c^2+v^2)^{1/2}.$ (7.12)

We have previously noted [Eq. (2.5)] the closed form

$$A(v,t)=e^{-t\rho\mu(v)}I_0(t\rho[\mu^2(v)-v^2]^{1/2}), \quad (7.13)$$

so that (7.9) becomes for these cases

I. $\frac{\partial}{\partial t}n_s(q,t)=\frac{c}{2}\frac{\partial^2}{\partial q^2}e^{-\rho ct}I_0[\rho(c^2t^2-q^2)^{1/2}], \quad$ for $|q|<ct$

$=0, \quad$ for $|q|>ct$

II. $\frac{\partial}{\partial t}n_s(q,t)=\frac{c^2t}{2}\frac{\partial^2}{\partial q^2}\left\{(c^2t^2+q^2)^{-1/2}I_0(\rho ct)\exp[-\rho(c^2t^2+q^2)^{1/2}]\right\}. \quad (7.14)$

Except for the wave front in I—significant at small time—due to a finite maximum velocity, these evince very similar forms in space and time. In fact, using the small and large argument expansions for I_0:

$I_0(x)=1+\frac{1}{4}x^2+\frac{1}{64}x^4+\cdots$ for small x

$\sim(2\pi x)^{-1/2}(1+(1/8x)+\cdots)e^x$ for large x (7.15)

together with (7.9) and (7.13), one finds

$$n_s(vt,t)=\frac{1}{2t}\frac{\partial^2}{\partial v^2}\left[\mu(v)+\frac{\rho t}{2}\mu^2(v)+\cdots\right] \quad \text{as} \quad t\rightarrow0, \quad (7.16)$$

extending the initial

$$n_s(q,t)\rightarrow\frac{1}{t}h_0\left(\frac{q}{t}\right) \quad \text{as} \quad t\rightarrow0, \quad (7.17)$$

obtained directly from (7.1) and (7.5). Similarly, at large time, we have

$$\frac{\partial}{\partial t}n_s(q,t)\sim\frac{1}{2}\frac{\mu(0)}{(2\pi\rho t)^{1/2}}\exp\left[-\frac{\rho}{2\mu(0)t}\left(q^2-\frac{1}{4\rho^2}+\cdots\right)\right] \quad (7.18)$$

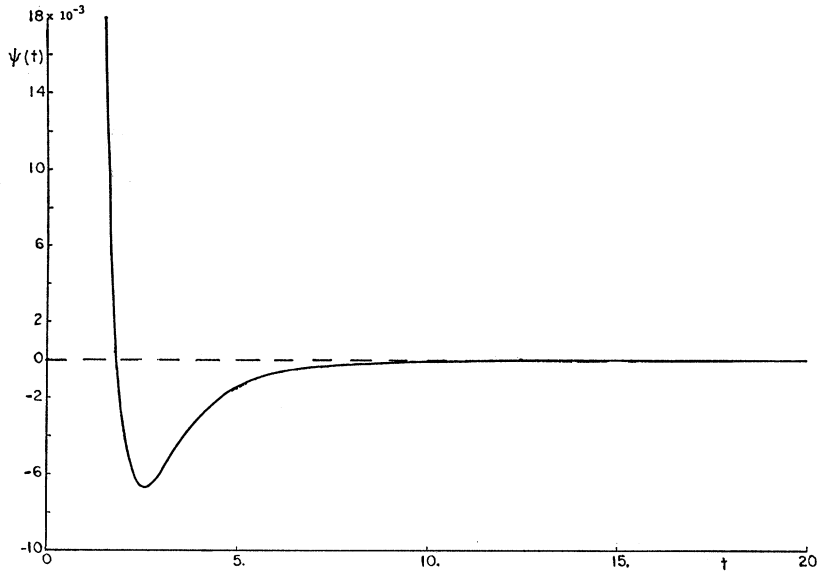depending to this order only on $\mu(0)$.

FIG. 2. Long-time behavior of velocity autocorrelation.

The full distribution n_s is then not a very sensitive test for distinguishing velocity distributions. One can say that both short- and long-time limits are Gaussian:

$$n_s(q,t) = [2\pi\sigma^2(t)]^{-1/2} \exp[-\tfrac{1}{2}q^2/\sigma^2(t)], \quad (7.19)$$

with the second spatial moment

$$\sigma^2(t) \equiv \int n_s(q,t)q^2 dq \qquad (7.20)$$

having the values

$$\sigma^2(t) \to \langle v^2 \rangle t^2 \qquad , \quad \text{as} \quad t \to 0$$
$$\to (1/\rho)\langle |v| \rangle t, \quad \text{as} \quad t \to \infty, \qquad (7.21)$$

and a transition time $T \sim 1/\rho\langle |v| \rangle$. This suggests a more careful perusal of the second moment, which according to (C13) of Appendix C, is also related to the velocity autocorrelation by

$$\psi(t) = \tfrac{1}{2}(\partial^2/\partial t^2)\sigma^2(t). \qquad (7.22)$$

From (7.9), we have at once

$$\frac{\partial}{\partial t}\sigma^2(t) = t\int [\mu(v) - v\mu'(v)]A(v,t)dv,$$

$$\psi(t) = \frac{1}{2}\frac{\partial}{\partial t}\left\{ t\int [\mu(v) - v\mu'(v)]A(v,t)dv \right\}, \qquad (7.23)$$

and these integrate out for our special cases I and II to

I. $\psi(t) = c^2 e^{-2\rho c t},$

II. $\psi(t) = +c^2(\partial/\partial t)[tI_0(c\rho t)K_0(c\rho t)].$ (7.24)

Now a qualitative distinction arises. The finite distribution I gives rise to a straight exponential decay, whereas the long-range case shows an asymptotic t^{-3}

dependence

$$\psi(t) \to \frac{-c^2}{8}\left[\frac{1}{(c\rho t)^3} + \frac{27}{16}\frac{1}{(c\rho t)^5} + \cdots \right] \qquad (7.25)$$

which persists for the shorter but not finite-range Maxwell distribution as well (Jepsen[8]). The short-time and long-time dependence of $\psi(t)$ in the Maxwellian case is shown in Figs. 1 and 2.

ACKNOWLEDGMENTS

APPENDIX A: THE TIME-DISPLACED PAIR DISTRIBUTION

Let us denote the phase point—coordinate and velocity—of a particle by $x = (r,v)$. An N-particle classical system of time-independent Hamiltonian H in a thermal ensemble will then have an equilibrium phase-space distribution

$$\mu_0(x_1, \cdots, x_N) = e^{-\beta H} \bigg/ \int \cdots \int e^{-\beta H} dx_1 \cdots dx_N \qquad (A1)$$

which is constant in time, as are the one- and two-body distribution functions

$$f_1(y_1) \equiv N \int \cdots \int \mu_0(x_1, \cdots, x_N)$$
$$\times \delta(x_1 - y_1)\prod dx_j, \qquad (A2)$$

$$f_2(y_1,y_2) \equiv N(N-1)\int \cdots \int \mu_0(x_1, \cdots, x_N)$$
$$\times \delta(x_1 - y_1)\delta(x_2 - y_2)\prod dx_j.$$

Now the prototype nonequilibrium behavior may be elicited by fixing the configuration of a single particle at time 0 (a convenient reference point; in an equilibrium canonical ensemble, only time differences are measurable). Thus μ has the initial value

$$\mu(\mathbf{x}_1,\cdots,\mathbf{x}_N; 0/\mathbf{y}_1)$$

$$=e^{-\beta H(\mathbf{x})}\delta(\mathbf{x}_1-\mathbf{y}_1)\Big/\int\cdots\int e^{-\beta H(\mathbf{z})}\delta(\mathbf{z}_1-\mathbf{y}_1)\prod d\mathbf{z}_j$$

$$=N\mu_0(\mathbf{x}_1,\cdots,\mathbf{x}_N)\delta(\mathbf{x}_1-\mathbf{y}_1)/f_1(\mathbf{y}_1) \qquad (A3)$$

and will evolve in time in accordance with the Liouville equation

$$(\partial\mu/\partial t)+(\mu,H)=0 \qquad (A4)$$

with (A3) as the initial condition. The one-body distribution

$$f_{1/1}(\mathbf{y}_2,t/\mathbf{y}_1)=(N-1)\int\cdots\int\mu(\mathbf{x}_1,\cdots\mathbf{x}_N; t/\mathbf{y}_1)$$
$$\times\delta(\mathbf{x}_2-\mathbf{y}_2)\prod dx_j \qquad (A5)$$

thereby expresses the conditional distribution of finding a particle at $\mathbf{y}_2$ at time t if it is known that a *different* particle was at $\mathbf{y}_1$ at time 0. Since the initial distribution of $\mathbf{y}_1$ is $f_1(\mathbf{y}_1)$, we conclude as well that

$$f_{1,1}(\mathbf{y}_2,t,\mathbf{y}_1,0)\equiv f_2(\mathbf{y}_2,t,\mathbf{y}_1)$$
$$=f_{1/1}(\mathbf{y}_2,t/\mathbf{y}_1)f_1(\mathbf{y}_1)\equiv f_2(\mathbf{y}_2,t/\mathbf{y}_1)f_1(\mathbf{y}_1) \qquad (A6)$$

represents the joint probability density of finding some particle at $\mathbf{y}_1$ and another at $\mathbf{y}_2$ at time t later.

If $\mathbf{x}_i(t)=\xi_i(t|\mathbf{x}_1\cdots\mathbf{x}_N)$ represents the explicit time dependence, following the equations of motion, $\dot{\mathbf{x}}_i=(\mathbf{x}_i,H)$, for a system of initial configuration $(\mathbf{x}_1\cdots\mathbf{x}_N)$, then the Liouville equation (A4) has the explicit (but generally highly complex and uncomputable) solution

$$\mu(\mathbf{x}_1,\cdots\mathbf{x}_N; t)=\mu(\cdots\xi_i(-t|\mathbf{x}_1\cdots\mathbf{x}_N)\cdots; 0), \qquad (A7)$$

so that

$$\int g(\mathbf{x}_1,\cdots\mathbf{x}_N)\mu(\mathbf{x}_1,\cdots\mathbf{x}_N; t)\prod dx_i$$

$$=\int g(\mathbf{x}_1(t),\cdots\mathbf{x}_N(t))\mu(\mathbf{x}_1,\cdots\mathbf{x}_N; 0)\prod dx_i. \qquad (A8)$$

In particular, then, from (A3), (A5), and (A6),

$$f_2(\mathbf{y}_2,t,\mathbf{y}_1)=N(N-1)\int\delta(\mathbf{x}_2(t)-\mathbf{y}_2)$$

$$\times\mu_0(\mathbf{x}_1,\cdots\mathbf{x}_N)\delta(\mathbf{x}_1-\mathbf{y}_1)\prod dx_i, \qquad (A9)$$

which we may rewrite in terms of equilibrium expectations as

$$f_2(\mathbf{y}_2,t,\mathbf{y}_1)=\Big\langle\sum_{i\neq j}\delta(\mathbf{x}_i(t)-\mathbf{y}_2)\delta(\mathbf{x}_j-\mathbf{y}_1)\Big\rangle. \qquad (A10)$$

In the same way, the self-distribution for some particle to be initially at $\mathbf{y}_1$ and then at $\mathbf{y}_2$ a time t later becomes

$$f_s(\mathbf{y}_2,t,\mathbf{y}_1)=\Big\langle\sum_i\delta(\mathbf{x}_i(t)-\mathbf{y}_2)\delta(\mathbf{x}_i-\mathbf{y}_1)\Big\rangle, \qquad (A11)$$

while the complete pair distribution, the joint probability for any particle to be initially at $\mathbf{y}_1$ and any (the same or a different one) at $\mathbf{y}_2$ at time t, is

$$\hat{f}_2(\mathbf{y}_2,t,\mathbf{y}_1)=f_2(\mathbf{y}_2,t,\mathbf{y}_1)+f_s(\mathbf{y}_2,t,\mathbf{y}_1)$$

$$=\Big\langle\sum_{i,j}\delta(\mathbf{x}_i(t)-\mathbf{y}_2)\delta(\mathbf{y}_j-\mathbf{x}_1)\Big\rangle. \qquad (A12)$$

When $t=0$, the time-displaced distributions reduce to the equilibrium distribution. For a uniform system (periodic boundary conditions or, in the thermodynamic limit $N\to\infty$, volume $\Omega\to\infty$, at fixed $N/\Omega=\rho$) the pair distributions depend only on the difference in position, e.g.,

$$\hat{f}_2(\mathbf{r}_2,\mathbf{v}_2,t,\mathbf{r}_1,\mathbf{v}_1)=\hat{f}_2(\mathbf{r}_2-\mathbf{r}_1, \mathbf{v}_2, t/\mathbf{v}_1)\rho h_0(\mathbf{v}_1). \qquad (A13)$$

Going to $t=0$, we then have, from (A10), (A11), and (A12),

$$\hat{f}_2(\mathbf{r}_1,\mathbf{v}_2,0/\mathbf{v}_1)=\rho g(\mathbf{r})h_0(\mathbf{v}_2)+\delta(\mathbf{r})\delta(\mathbf{v}_2-\mathbf{v}_1),$$
$$f_2(\mathbf{r},\mathbf{v}_2,0/\mathbf{v}_1)=\rho g(\mathbf{r})h_0(\mathbf{v}_2), \qquad (A14)$$
$$f_s(\mathbf{r},\mathbf{v}_2,0/\mathbf{v}_1)=\delta(\mathbf{v})\delta(\mathbf{v}_2-\mathbf{v}_1),$$

where $g(\mathbf{r})$ is the usual radial distribution function. However, for $t\neq0$, f_s in general depends as well on the dynamics of the system, and no "universal" component of $\hat{f}_2$ can meaningfully be isolated.[4] The ideal-gas case (no interaction between the particles) is still simple, for it is seen at once that $f_2(\mathbf{r},\mathbf{v}_2,t/\mathbf{v}_1)$ is independent of time, while $g(\mathbf{r})=[1-1/N]\to 1$ as $N\to\infty$, so that

$$f_2(\mathbf{r},\mathbf{v}_2,t/\mathbf{v}_1)=\rho h_0(\mathbf{v}_2)$$

whereas

$$f_s(\mathbf{r},\mathbf{v}_2,t/\mathbf{v}_1)=\delta(\mathbf{r}-\mathbf{v}_2 t)\delta(\mathbf{v}_2-\mathbf{v}_1). \qquad (A15)$$

The system considered by Jepsen (one-dimensional hard rods of zero diameter) has the same equilibrium properties as an ideal gas, and the whole dynamics of the system consists of the interchange of particle velocities during a collision. This is completely equivalent to the interchange of the labeling of the colliding particles. Hence all system properties which do not depend on particle labeling, e.g., $\hat{f}_2$, are identical with those found for the ideal gas:

$$\hat{f}_2(r,v_2,t/v_1)=\rho h_0(v_2)+\delta(r-v_2 t)\delta(v_2-v_1). \qquad (A16)$$

The decomposition however no longer corresponds to that into f_2 and f_s, which must now be computed from the dynamics.

APPENDIX B: EVALUATION OF TIME-DISPLACED DISTRIBUTIONS

Consider N point particles on a line of length L in the limit $L\to\infty$ at fixed $\rho=N/L$. We are interested in the

development of the conditional p-body distribution at v_0 at the origin at time $t=0$. This is defined by the
time t when it is known that there is a particle of velocity $N \to \infty$ limit of

$$\hat{f}_{p/1}(q_1,v_1,q_2,v_2,\cdots,q_p,v_p,t/v_0) = \sum_i \sum_{j_1 \neq \cdots j_p} \langle \delta(v_i - v_0) \delta(r_{j_1}(t) - r_i - q_1)$$

$$\times \delta(v_{j_1}(t) - v_1) \cdots \delta(r_{j_p}(t) - r_i - q_p) \delta(v_{j_p}(t) - v_p) \rangle / N h_0(v_0) . \quad (B1)$$

The corresponding self-distribution is

$$f_{p/1s}(q_1,v_1,q_2,v_2,\cdots,q_p,v_p,t/v_0) = \sum_{j_1 \neq \cdots j_p} \langle \delta(v_{j_1} - v_0) \delta(r_{j_1}(t) - r_{j_1} - q_1)$$

$$\times \delta(v_{j_1}(t) - v_1) \cdots \delta(r_{j_p}(t) - r_{j_1} - q_p) \delta(v_{j_p}(t) - v_p) \rangle / N h_0(v_0) , \quad (B2)$$

in which the first of the p bodies is the initial distinguished particle. If the particles are zero-diameter hard cores, they merely reflect on collision, maintaining the pair of trajectories but interchanging identity. Thus a symmetric quantity, such as $\hat{f}_{p/1}$, reduces to its free-particle form:

$$\hat{f}_{p/1}(q_1,v_1,\cdots,q_p,v_p,t/v_0) = \rho^p \prod_{\alpha=1}^{p} h_0(v_\alpha) \left[1 + \sum_{\alpha=1}^{p} \frac{\delta(q_\alpha - v_0 t)}{\rho} \frac{\delta(v_\alpha - v_0)}{h_0(v_\alpha)} \right]. \quad (B3)$$

To determine the self-distribution $f_{p/1s}$, free-particle trajectories may also be used providing that we identify the particle represented by $r_{j_1}(t)$ with the same particle r_{j_1} at time 0. Since the particle ordering does not change on collision, this can be achieved by specifying that its order

$$\sigma_i \equiv \sum_l \epsilon(r_i - r_l) \quad (B4)$$

is unchanged in time. Hence (B2) may be replaced by

$$f_{p/1s}(q_1,v_1,\cdots,q_p,v_p,t/v_0) = \sum_i \sum_{j_1 \neq \cdots j_p} \langle \delta(v_i - v_0) \delta(r_{j_1}(t) - r_i - q_1)$$

$$\times \delta(v_{j_1}(t) - v_1) \cdots \delta(r_{j_p}(t) - r_i - q_p) \delta(v_{j_p}(t) - v_p) \delta_{\sigma_{j_1}(t),\sigma_i} \rangle / N h_0(v_0) , \quad (B5)$$

where the dynamics proceeds according to

$$v_i(t) = v_i , \quad r_i(t) = r_i + v_i t . \quad (B6)$$

In order to evaluate (B5), we employ a Fourier representation of the Kronecker δ function:

$$\delta_{\sigma_{j_1}(t),\sigma_i} = \frac{1}{2\pi} \int_0^{2\pi} \exp[i\theta(\sigma_{j_1}(t) - \sigma_i)] d\theta = \frac{1}{2\pi} \int \exp\left[i\theta \sum_l \{\epsilon[r_{j_1}(t) - r_l(t)] - \epsilon(r_i - r_l)\} \right] d\theta . \quad (B7)$$

Now the particles are independent, so that only the expectation

$$E_t(r_j - r_i, \theta) \neq \langle \exp(i\theta\{\epsilon[r_j(t) - r_l(t)] - \epsilon(r_i - r_l)\}) \rangle_{r_l,v_l} \quad (B8)$$

with respect to the lth particle is required, where $l \neq i$, $j_1, \cdots j_p$. Separating (B5) into two parts according to whether $i \neq j_1, \cdots j_p$ or the converse, we then have

$$f_{p/1s}(q_1,v_1,\cdots,q_p,v_p,t/v_0) = f_{p+1}{}^0(q_1,v_1,\cdots,q_p,v_p,t; 0,v_0)/\rho h_0(v_0)$$

$$\times \frac{1}{2\pi} \int E_t(q_1,\theta)^{N-p-1} \exp i\theta[\epsilon(q_1 - v_0 t) - \epsilon(v_1 t - q_1)] \exp\{i\theta \sum_2^p [\epsilon(q_1 - q_\alpha) - \epsilon(v_\alpha t - q_\alpha)]\} d\theta$$

$$+ [f_{p/1}{}^0(q_1,v_1,\cdots q_p,v_p,t/v_0) - f_{p+1}{}^0(q_1,v_1,\cdots q_p,v_p,t; 0,v_0)/\rho h_0 v_0)]$$

$$\times \frac{1}{2\pi} \int E_t(q_1,\theta)^{N-p} \exp\{i\theta \sum_2^p [\epsilon(q_1 - q_\alpha) - \epsilon(v_\alpha t - q_\alpha)]\} d\theta , \quad (B9)$$

where superscript zero denotes free-particle motion.

There remains the computation of $E_t(q,\theta)$. But

$$\exp[i\theta[\epsilon(x)-\epsilon(y)]] = 1 + [\epsilon(x)-\epsilon(y)]i\,\sin\theta - \epsilon(-xy)(1-\cos\theta) \tag{B10}$$

so that

$$E_t(r_j-r_i,\ \theta) = 1 + \langle r_j(t)-r_i-v_i t\rangle_{v_i}(i/L)\sin\theta - \langle|r_j(t)-r_i-v_i t|\rangle_{v_i}(1/L)(1-\cos\theta). \tag{B11}$$

Averaging over v_i with the assumption $\langle v_i\rangle = 0$, and defining

$$\mu(w) = \langle|w-v_i|\rangle_{v_i}, \tag{B12}$$

we have

$$E_t(q,\theta) = 1 + (iq/L)\sin\theta - [t\mu(q/t)/L](1-\cos\theta). \tag{B13}$$

Only the Nth power of $E_t(q,\theta)$ is required in the $N\to\infty$ limit. We then define

$$F(t\rho,\theta,v) = E_t(tv,\theta)^N = \exp\{-t\rho[\mu(v)(1-\cos\theta)-iv\,\sin\theta]\} \tag{B14}$$

and use (B3) together with the free-particle unconditional joint distribution

$$f_{p+1}{}^0(q_1,v_1,\cdots q_p,v_p,t;\,0,v_0) = \rho^{p+1}\prod_{\alpha=0}^{p} h_0(v_\alpha) \tag{B15}$$

to complete the evaluation of $f_{p/1s}$, obtaining

$$f_{p/1s}(q_1,v_1,\cdots,q_p,v_p,t/v_0) = [\rho^p\prod_1^p h_0(v_\alpha)]\frac{1}{2\pi}\int F(t\rho,\theta,q_1/t)\exp(i\theta[\epsilon(q_1-v_0 t)-\epsilon(v_1 t-q_1)])$$

$$\times\exp(i\theta\sum_2^p[\epsilon(q_1-q_\alpha)-\epsilon(v_\alpha t-q_\alpha)])d\theta + (\rho^p\prod_1^p h_0(v_\alpha))\left(\sum_1^p\frac{\delta(v_\alpha-v_0)\delta(q_\alpha-v_\alpha t)}{h_0(v_\alpha)}\right)$$

$$\times\frac{1}{2\pi}\int F(t\rho,\theta,q_1/t)\exp(i\theta\sum_1^p[\epsilon(q_1-q_\alpha)-\epsilon(v_\alpha t-q_\alpha)])d\theta. \tag{B16}$$

The lower-order distributions are of special interest. Choosing $p=1$, we have the usual conditional self-distribution

$$f_s(q,v,t/v') = \delta(v-v')\delta(q-vt)\frac{1}{2\pi}\int F(t\rho,\theta,q/t)\,d\theta + \rho h_0(v)\frac{1}{2\pi}\int F(t\rho,\theta,q/t)\exp(i\theta[\epsilon(q-v't)-\epsilon(vt-q)])d\theta. \tag{B17}$$

Somewhat more explicitly, bringing down the step functions from the exponents,

$$f_s(q,v,t/v') = [\rho h_0(v)+\delta(v-v')\delta(q-vt)]A_0(q/t,t)$$
$$+\rho h_0(v)\epsilon(q-v't)\epsilon(q-vt)[A_1(q/t,t)-A_0(q/t,t)]+\rho h_0(v)\epsilon(v't-q)\epsilon(vt-q)[A_{-1}(q/t,t)-A_0(q/t,t)], \tag{B18}$$

where

$$A_l(v,t)\equiv\frac{1}{2\pi}\int F(t\rho,\theta,v)e^{il\theta}d\theta. \tag{B19}$$

Further simplification then results from the observation that

$$(e^{\pm i\theta}-1)F(t\rho,\theta,v) = \frac{1}{\rho}\left(\frac{\partial}{\partial t\mu(v)}\pm\frac{\partial}{\partial tv}\right)F(t\rho,\theta,v). \tag{B20}$$

In the form (B18), we can readily take the Fourier-Laplace transform:

$$K(k,s;v,v')\equiv\int_{-\infty}^{\infty}\int_0^{\infty} e^{ikq}e^{-st}f_s(q,v,t/v')\,dt\,dq = \int\int e^{-(s-ikw)t}\left\{\delta(v-v')\delta(w-v)\right.$$

$$\left.+h_0(v)\left[t\rho+\epsilon(w-v')\epsilon(w-v)t\left(\frac{\partial}{\partial t\mu(v)}+\frac{\partial}{\partial tv}\right)+\epsilon(v'-w)\epsilon(v-w)t\left(\frac{\partial}{\partial t\mu(v)}-\frac{\partial}{\partial tv}\right)\right]\right\}A_0(w,t)\,dt\,dw. \tag{B21}$$

Noting that, with respect to the Laplace transform,

$$t\left(\frac{\partial}{\partial t\mu(v)}\pm\frac{\partial}{\partial tv}\right)=[v\mu'(v)-\mu(v)]^{-1}\left[(v\mp\mu(v))\frac{\partial}{\partial v}-(1\mp\mu'(v))t\frac{\partial}{\partial t}\right]\to[v\mu'(v)-\mu(v)]^{-1}\left[(v\mp\mu(v))\frac{\partial}{\partial v}+(1\mp\mu'(v))\frac{\partial}{\partial s}s\right],$$

(B22)

and that

$$\tilde{A}(v,s)\equiv\int_0^\infty e^{-st}A_0(v,t)dt=(\rho^2 v^2+2s\rho\mu(v)+s^2)^{-1/2},$$

(B23)

(B21) yields after minor algebraic operations

$$K(k,s; v,v')=\delta(v-v')\tilde{A}(v, s-ikv)+\rho h_0(v)\int_{-\infty}^{\infty}[(s-ikw+\rho\mu(w))$$

$$-(s-ikw+\rho w)\epsilon(w-v')\epsilon(w-v)-(s-ikw-\rho w)\epsilon(v'-w)\epsilon(v-w)][\tilde{A}(w,s-ikw)]^3 dw.$$

(B24)

When $p=2$, we have from (B16)

$$f_{2/1s}(q,v,q',v',t/c)=\rho^2 h_0(v)h_0(v')\frac{1}{2\pi}\int F(t\rho,\theta,q/t)\exp\{i\theta[\epsilon(q-ct)-\epsilon(vt-q)]\}$$

$$\times\exp\{i\theta[\epsilon(q-q')-\epsilon(v't-q')]\}d\theta+\rho(h_0[v]\delta(v'-c)\delta(q'-ct)+h_0(v')\delta(v-c)\delta(q-ct)]$$

$$\times\frac{1}{2\pi}\int F(t\rho,\theta,q/t)\exp\{i\theta[\epsilon(q-q')-\epsilon(v't-q)]\}\exp\{i\theta[\epsilon(0)-\epsilon(vt-q)]\}d\theta.$$

(B25)

In particular, at right and left contact, $q'=q^+$ or $q'=q^-$, we have

$$f_{(+)}(q,v,v',t/c)=\rho^2 h_0(v)h_0(v')\frac{1}{2\pi}\int F(t\rho,\theta,q/t)$$

$$\times\exp\{i\theta[\epsilon(q-ct)-\epsilon(vt-q)-\epsilon(v't-q)]\}d\theta+\rho h_0(v')\delta(v-c)\delta(q-ct)\frac{1}{2\pi}\int F(t\rho,\theta,q/t)\exp[-i\theta\epsilon(v'-v)]d\theta$$

$$+\rho h_0(v)\delta(v'-c)\delta(q-ct)\frac{1}{2\pi}\int F(t\rho,\theta,q/t)\exp[-i\theta\epsilon(v-v')]d\theta,$$

(B26)

with F replaced by $Fe^{i\theta}$ to obtain $f_{(-)}$. Rewriting (B26) in the form

$$f_{(+)}(q,v,v',t/c)=\rho^2 h_0(v)h_0(v')\{A_0(q/t,t)+\epsilon(q-ct)\epsilon(q-vt)\epsilon(q-v't)[A_1(q/t,t)-A_0(q/t,t)]$$
$$+[\epsilon(q-ct)\epsilon(vt-q)\epsilon(v't-q)+\epsilon(ct-q)\epsilon(vt-q)+\epsilon(ct-q)\epsilon(v't-q)][A_{-1}(q/t,t)-A_0(q/t,t)]$$
$$+\epsilon(ct-q)\epsilon(vt-q)+\epsilon(v't-q)[A_{-2}(q/t,t)-2A_{-1}(q/t,t)+A_0(q/t,t)]\}$$
$$+\rho\delta(q-ct)[h_0(v')\delta(v-c)+h_0(v)\delta(v'-c)]A_0(q/t,t)$$
$$+\rho\delta(q-ct)[h_0(v')\delta(v-c)\epsilon(v'-v)+h_0(v)\delta(v'-c)\epsilon(v-v')][A_{-1}(q/t,t)-A_0(q/t,t)],$$

(B27)

and combining with (B18), we may write

$$f_{(+)}(q,v,v',t/c)=\rho\epsilon(v-v')[h_0(v')f_s(q,v,t/c)+h_0(v)W(q,v',t/c)]+\rho\epsilon(v'-v)[h_0(v)f_s(q,v',t/c)+h_0(v')W(q,v,t/c)],$$

(B28)

where

$$W(q,v,t/c)=\rho h_0(v)\epsilon(vt-q)\left\{[A_{-1}(q/t,t)-A_0(q/t,t)]\right.$$

$$\left.+\epsilon(ct-q)[A_{-2}(q/t,t)-2A_{-1}(q/t,t)+A_0(q/t,t)]\right\}+\delta(v-c)\delta(q-ct)A_{-1}(q/t,t).$$

(B29)

The Fourier-Laplace transform of (B29) is obtainable as in (B21)–(B24). We find

$$W(k,s; v,c) = \delta(v-c)\left\{\frac{[s-ikv+\rho\mu(v)]\tilde{A}(v, s-ikv)-1}{\mu(v)-v}+\tilde{A}(v, s-ikv)\right\}$$

$$-\rho h_0(v)\int \epsilon(v-w)(s-ikw-\rho w)[\tilde{A}(w, s-ikw)]^3 dw$$

$$+\rho h_0(v)\int \epsilon(v-w)\epsilon(c-w)\left[\frac{2}{(\mu(w)-w)^2}-\frac{2(s-ikw)+\rho(\mu(w)+w)}{(\mu(w)-w)^2}\tilde{A}(w, s-ikw)\right.$$

$$\left.-\frac{(s+\rho\mu(w)-ikw)(s-\rho w-ikw)}{\mu(w)-w}[\tilde{A}(w, s-ikw)]^3\right]dw. \quad (B30)$$

APPENDIX C: SELF-DIFFUSION IN A RANDOMIZED BACKGROUND

The coefficient of self-diffusion in a one-dimensional system may be written as—for a given test particle—

$$D=\int_0^\infty \langle v(0)v(t)\rangle dt, \quad (C1)$$

or when the integral is not absolutely convergent, as

$$D=\lim_{\gamma\to 0}\int_0^\infty e^{-\gamma t}\langle v(0)v(t)\rangle dt. \quad (C2)$$

Hence we also have

$$D=\langle vR_\infty(v)\rangle, \quad (C3)$$

where the diffusion length at velocity v is defined by

$$R_\infty(v)=\lim_{\gamma\to 0}\int_0^\infty e^{-\gamma t}\langle v(t)\,|\,v(0)=v\rangle dt. \quad (C4)$$

Now if the medium is specified by an ensemble of infinitely massive scatterers,[17] the velocity will change sign at each scattering time, depending only on the position of the left and right nearest neighbors. If we denote the first scattering time by T_0, and the successive intervals between scattering by $\Delta_1, \Delta_2, \cdots$, then

$$\int_{T_0+\Sigma_1{}^{m-1}\Delta_i}^{T_0+\Sigma_1{}^m\Delta_i} e^{-\gamma t}dt$$

$$=\frac{1}{\gamma}e^{-\gamma T_0}[\exp(-\gamma\sum_1^{m-1}\Delta_i)-\exp(-\gamma\sum_1^m\Delta_i)],$$

so that (C4) becomes

$$R_\infty(v)=\lim\frac{v}{\gamma}\langle 1-2e^{-\gamma T_0}\sum_0^\infty (-1)^m \exp(-\gamma\sum_1^m\Delta_i)\rangle. \quad (C5)$$

[17] See also R. Nossal, J. Math. Phys. **6**, 201 (1965).

For a stationary process (homogeneous in time) the distribution of T_0 is uniform from 0 to Δ_0, so that

$$\langle f(T_0,\Delta_1,\Delta_2,\cdots)\rangle=\left\langle\int_0^1 f(t\Delta_0,\Delta_1,\Delta_2\cdots)dt\right\rangle \quad (C6)$$

(e.g., $\langle T_0\rangle=\frac{1}{2}\langle\Delta_0\rangle$) and (C5) may be written as

$$R_\infty(v)=\lim\frac{v}{\gamma}\int_0^1\langle 1-2e^{-t\gamma\Delta_0}\sum_0^\infty (-1)^m$$

$$\times\exp(-\gamma\sum_1^m\Delta_i)\rangle dt. \quad (C7)$$

To evaluate (C7), let us introduce the generating function

$$\langle e^{-t_0\Delta_0}e^{-t_1\Delta_1}\cdots e^{-t_n\Delta_n}\rangle=\exp-[\sum_0^n \phi_1(t_i)$$

$$+\sum_0^{n-1} \phi_2(t_i,t_{i+1})+\sum_0^{n-2} \phi_3(t_i,t_{i+1},t_{i+2})+\cdots], \quad (C8)$$

where only ϕ_1 exists for independent intervals, ϕ_2 introduces a Markoffian character, etc. Equation (C7) now becomes

$$R_\infty(v)=\lim\frac{v}{\gamma}\int_0^1\langle 1-2\exp[-\phi_1(t\gamma)]$$

$$\times\Big\{1-\exp[-\phi_1(\gamma)-\phi_2(t\gamma,\gamma)]$$

$$\times[1-\exp\{-[\phi_1(\gamma)+\phi_2(\gamma,\gamma)]\}$$

$$+\exp\{2[\phi_1(\gamma)+\phi_2(\gamma,\gamma)]\}-\cdots]\Big\}\rangle dt$$

$$+(v/\gamma)0(\phi_3,\phi_4,\cdots), \quad (C9)$$

or, if $\gamma^{-1}0(\phi_3,\phi_4,\cdots)\to 0$ as $\gamma\to 0$,

$$R_\infty(v)=\lim\frac{v}{\gamma}\int_0^1\Big\langle 1-2\exp[-\phi_1(t\gamma)]$$

$$\times\Big[1-\frac{\exp[-\phi_1(\gamma)-\phi_2(t\gamma,\gamma)]}{1+\exp[-\phi_1(\gamma)-\phi_2(\gamma,\gamma)]}\Big]\Big\rangle dt. \quad (C10)$$

Noting that $\phi_1(0)=\phi_2(0,0)=0$ and defining

$$\bar{\Delta}=\phi_1'(0),\quad \delta=-\phi_2'(\gamma,0)\big|_{\gamma=0}, \quad (C11)$$

Eq. (C10) is readily evaluated. We find

$$R_\infty(v)=\tfrac{3}{2}v\delta, \quad (C12)$$

independently of $\bar{\Delta}=\langle\Delta_i\rangle$. Thus, if the intervals are independent, $R_\infty(v)=0$. Moreover, if the scattering ensemble is not just homogeneous in time but static, so that

$$\langle\exp(-t_0\Delta_0)\cdots\exp(-t_n\Delta_n)\rangle$$

$$=\langle\exp-\sum_0^n t\Delta_i\rangle_\Delta=\exp-\phi(\sum_0^n t_i),$$

then $\phi_1(t)=\phi(t)$; $\phi_2(t)=\phi(t_1+t_2)-\phi(t_1)-\phi(t_2)=0(\gamma^2)$ for $t_1,t_2=0(\gamma)$; $\phi_3=0(\gamma^3)$, etc. Thus again $R_\infty(v)=0$. It is only for partially correlated successive time intervals that $\delta\neq0$ and $R_\infty(v)\neq0$.

From another viewpoint, we see by virtue of

$$\langle v(0)v(t)\rangle=\langle v(t')v(t+t')\rangle=\frac{\partial}{\partial t}\Big(\frac{\partial}{\partial t'}-\frac{\partial}{\partial t}\Big)\langle r(t')r(t+t')\rangle$$

$$=-\frac{\partial^2}{\partial t^2}\langle r(t')r(t+t')\rangle$$

$$=-\frac{\partial^2}{\partial t^2}\langle r(0)r(t)\rangle=\frac{1}{2}\frac{\partial^2}{\partial t^2}\langle[r(t)-r(0)]^2\rangle$$

coupled with (C2) that

$$D=\frac{1}{2}\frac{\partial}{\partial t}\langle[r(t)-r(0)]^2\rangle\Big|_{t\to\infty}. \quad (C13)$$

For a static scattering ensemble, $\langle(r(t)-r(0))^2\rangle$ will not grow in time, and so, of course, $D=0$.