PHYSICAL REVIEW A VOLUME 9, NUMBER 3 MARCH 1974

Persistent correlations in diffusion

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(Received 27 June 1973)

The effect of persistent correlations on self-diffusion in a dilute gas, and on Brownian motion, is discussed. It is found in both cases that the second-order diffusion constant is infinite. The distribution function for displacements is calculated, and is found to be more sharply peaked than the usual Gaussian, although the difference is quite small.

The persistent correlation of velocity first observed in computer experiments by Alder and Wainwright[1] has attracted considerable attention because it contradicts, in a basic way, predictions of classical kinetic theory. One symptom of this is the nonexistence in two dimensions of the coefficient of diffusion.[1] In three dimensions, Ernst and Dorfman[2] have shown that the dependence of the hydrodynamic frequencies on wave number is not analytic, implying that higher-order diffusion constants do not exist.

The purpose of this paper is to consider further the consequences of persistent correlations for diffusion. The second-order diffusion constant is calculated for the case of self-diffusion in a gas by use of the ring operator,[3] and for the case of Brownian motion by use of a frequency-dependent friction constant. In both cases the second-order diffusion constant is infinite, in agreement with the results of Ernst and Dorfman.[2] To describe the nature of the infinity, consider the usual diffusion length l, defined by

$$l=[\langle x^2\rangle]^{1/2}, \tag{1}$$

where x is the displacement of the particle in the x direction during time t and the angular brackets denote an equilibrium average. If the ordinary diffusion constant D is finite then, as is well known, l increases with increasing time as $t^{1/2}$. The second-order diffusion constant D_2 is related to a diffusion length l_2 defined by[4]

$$l_2=[\langle x^4\rangle-3\langle x^2\rangle^2]^{1/4}. \tag{2}$$

If D_2 is finite, then l_2 should increase with time as $t^{1/4}$, but it is found instead that the increase is as $t^{3/8}$, implying that D_2 is infinite. However, l_2 is considerably smaller than l, and so the anomalous behavior of D_2 might be difficult to observe.

A nonvanishing l_2 implies a deviation from a Gaussian distribution of displacements. Consequently, the distribution function for displacements is calculated below, again for the two cases of self-diffusion in a gas and for Brownian motion. It is found that the distribution function is more sharply peaked than a Gaussian, but the difference in both cases is quite small.

Let n denote the density of diffusing particles. The diffusion equation with higher-order terms can be written

$$\frac{\partial n}{\partial t}=D\nabla^2 n+D_2\nabla^2\nabla^2 n+\ldots. \tag{3}$$

The diffusion constant D is given by the Einstein formula

$$D=\lim_{t\to\infty}\langle x^2\rangle/2t. \tag{4}$$

The second-order diffusion constant D_2 is given by a similar formula,[4]

$$D_2=\lim_{t\to\infty}Q(t)/4!\,t, \tag{5}$$

where

$$Q(t)=\langle x^4\rangle-3\langle x^2\rangle^2 = l_2^4. \tag{6}$$

The moments of displacement can be obtained from the generating function

$$G(k,t)=\langle e^{ikx}\rangle. \tag{7}$$

For self-diffusion in a gas, the Laplace transform

$$\overline{G}(k,p)=\int_0^\infty e^{-pt}G(k,t)\,dt \tag{8}$$

has been calculated from the ring operator by Dufty[5] to Navier-Stokes order. That calculation is extended here to (super) Burnett order, or order k^4. The low-density limit of the ring approximation to $\overline{G}(k,p)$ is given by

$$\overline{G}(k,p)=(1,R1), \tag{9}$$

where the scalar product (a,b) is defined by

$$(a, b) = \int dv f_0(v) a^*(v) b(v)$$

and $f_0(v)$ is the Maxwell-Boltzmann distribution. The resolvent operator R is given by

$$R = (p + i\vec{k}\cdot\vec{v} + nJ - n\mathcal{B})^{-1}. \quad (10)$$

Here nJ is the Boltzmann-Lorentz collision operator and $n\mathcal{B}$ is the ring operator,

$$n\mathcal{B} = n\int \frac{d\vec{k}'}{(2\pi)^3}\int d\vec{v}_2 f_0(v_2)\langle 0,0|t_{12}|0,0\rangle \times K(12)\langle 0,0|t_{12}|0,0\rangle, \quad (11)$$

$$K(12) = [p + ik'\cdot v_1 + i(k-k')\cdot v_2 + nJ + nI_2]^{-1}.$$

Also, nI is the linearized Boltzmann operator. The subscripts 1 and 2 indicate that the domain of the operators is a function of v_1 or v_2, respectively. Explicit form for the two-body operators, t_{12}, may be found in the literature.[3] To evaluate expression (9) for small k, p we assume the existence of solutions to the eigenvalue problem,

$$(i\vec{k}\cdot\vec{v} + nJ - n\mathcal{B})g(k,p,v) = \lambda(k,p)g(k,p,v), \quad (12)$$

with

$$\lim_{k\to 0} g(k,p,v) = 1,$$
$$\lim_{k\to 0}\lambda(k,p) = 0.$$

This assumption is based on the fact that 1 is an eigenfunction with zero eigenvalue for $k=0$. For $k\neq 0$ the operator $n\mathcal{B}$ is not self-adjoint, so the equation adjoint to (12) must also be considered. The generating function $\overline{G}(k,p)$ may be expressed in terms of $g(k,p,v)$ and $\lambda(k,p)$ as

$$\overline{G}(k,p,v) = \frac{(1,g)(\tilde{g},1)}{(\tilde{g},g)[p+\lambda(k,p)]} + (1_\perp, R1_\perp), \quad (13)$$

where $\tilde{g}$ is the biorthogonal compliment of g and

$$1_\perp = 1 - g(\tilde{g},1)/(\tilde{g},g).$$

The first term in Eq. (13) is the "hydrodynamic part" and gives the dominant contribution to $G(k,t)$ for long times. Only the hydrodynamic part will be considered in the following. The eigenfunction g and the eigenvalue λ will be calculated by perturbation theory. Since $G(k,t)$ is required to order k^4, to determine the mean fourth displacement the perturbation expansion is required to fourth order. The perturbation expansion is carried out in the Appendix, with the results

$$(g,g) = 1 - a(p)k^2 + b(p)k^4 + \cdots$$
$$= \lambda_2(p)k^2 + \lambda_4(p)k^4 + \cdots. \quad (14)$$

Since the long-time behavior of $G(k,t)$ is determined from the small-p behavior of $\overline{G}(k,p)$ only the corresponding asymptotic behavior of a, b, λ_2, and λ_4 is needed. The results found in the Appendix are

$$a(p) \to m\lambda_2^2/T,$$
$$\lambda_2(p) \to D_0(1 - Bp^{1/2}),$$
$$\lambda_4(p) \to \frac{-BD_0^2(\nu + 2/5D_0)}{p^{1/2}\alpha(D_0+\nu)}, \quad (15)$$
$$b(p) \to 2\lambda_4 D_0.$$

Here D_0 is the coefficient of self-diffusion as determined from the Boltzmann equation, T is the Kelvin temperature (in units such that the Boltzmann constant is equal to 1), ν is the kinematic viscosity of the gas, ρ its mass density, and the constant B is

$$B = T[6\pi\rho D_0(\nu + D_0)^{3/2}]^{-1}. \quad (16)$$

The hydrodynamic part of $\overline{G}(k,p)$ is therefore, to this order,

$$\overline{G}^h(k,p) = [(1 - ak^2 + bk^4)(p + \lambda_2 k^2 + \lambda_4 k^4)]^{-1}. \quad (17)$$

The dependence of a, b, λ_2, and λ_4 on p has been left implicit.

It is straightforward to obtain $\langle x^2\rangle$ and $\langle x^4\rangle$ from the generating function (7) by expanding in powers of k. Using the form (17), one obtains first the Laplace transform of $\langle x^2\rangle$ and $\langle x^4\rangle$ as

$$\mathcal{L}\langle x^2\rangle = \frac{-2}{p}\left(a - \frac{\lambda_2}{p}\right),$$
$$\mathcal{L}\langle x^4\rangle = \frac{4!}{p}\left[\left(\frac{\lambda_2}{p}\right)^2 - \frac{\lambda_4 + \lambda_2 a}{p} - (b - a^2)\right], \quad (18)$$

where $\mathcal{L}$ denotes the Laplace transform. Inversion of the transform in Eq. (18), with expression (15), gives for long times

$$\langle x^2\rangle \to 2D_0 t - 4BD_0(t/\pi)^{1/2},$$
$$\langle x^4\rangle \to 4!\left(\frac{D_0 t^2}{2} - t^{3/2}\frac{2D_0^2 B(6D_0 + 5\nu)}{5\pi^{1/2}(D_0+\nu)}\right). \quad (19)$$

This yields for $Q(t)$

$$Q(t) \to -(8/5\pi^{3/2})(D_0^2 T/\rho)(D_0+\nu)^{-5/2}t^{3/2}. \quad (20)$$

Since $Q(t)$ increases as $t^{3/2}$, it follows immediately that D_2 is infinite. There are no contributions from $a(p)$ or $b(p)$ to the asymptotic limit of $Q(t)$, so that actually only the eigenvalue λ needs to be calculated to Burnett order. Furthermore, the evaluation of λ_4 in the Appendix shows that only the Navier-Stokes-order modes for the gas are required in determination of the contributions from the ring operator. Specifically, it is the coupling of Navier-Stokes-order modes which leads to the most divergent part of the Burnett self-diffusion constant.

Parameters for a gas of hard spheres with diameter d and mass m can be introduced by[6]

$$D_0 = T/mf, \quad \nu = 6D_0/5. \tag{21}$$

Here f is the collision frequency, given by

$$f = (8\rho d^2/3m)(\pi T/m)^{1/2}. \tag{22}$$

The result for $Q(t)$ is

$$Q(t) = -c(d^4/y^2)(ft)^{3/2}, \tag{23}$$

where $c = (16/15)(5/11)^{5/2} = 0.149$ and $y = 4\pi\rho d^3/3m$. As a numerical example, consider $ft = 10$, $y = 0.1$, then $l_2 = 4.7d$, while for comparison $l = 39.6d$. Evidently quite large times are necessary for the divergence of D_2 to become apparent.

Consider next Brownian motion. The ring operator has been derived only for a gas of equal particles, and so we will proceed by the *ad hoc* introduction of a frequency-dependent friction constant. The persistent correlations can be described by a modified Langevin equation[7] in which the dynamic drag force is used in place of the Stokes force as follows[8]:

$$\frac{dv}{dt} = -\xi_0 v - \mu \frac{dv}{dt} - \xi_0 a(\pi\nu)^{-1/2} \times \int_{-\infty}^{t} ds\,(t-s)^{-1/2}\frac{dv}{ds} + A(t). \tag{24}$$

Here $A(t)$ is the random force, and the Stokes-law friction constant ξ_0 is given by

$$\xi_0 = 6\pi\eta a/m, \tag{25}$$

where $\eta = \rho\nu$ is the viscosity of the fluid, a is the radius of the particle, and m its mass. We will treat only one component of the particle's motion, and so v denotes its velocity in the x direction. The coefficient μ in Eq. (24) describes the effective mass of the particle, and is given by

$$\mu = 2\pi\rho a^3/3m; \tag{26}$$

for Brownian motion of particles in a gas this term is negligible and will henceforth be neglected.

Let $\chi(t)$ denote the velocity autocorrelation,

$$\chi(t) = \langle vv(t)\rangle/\langle v^2\rangle. \tag{27}$$

Then $\chi(t)$ can be obtained from Eq. (24) by taking the Laplace transform. One finds[7]

$$\mathfrak{L}\chi(t) = [p + \xi(p)]^{-1}, \tag{28}$$

where, with the approximation $\mu = 0$,

$$\xi(p) = \xi_0[1 + a(p/\nu)^{1/2}]. \tag{29}$$

In the usual theory based on Langevin's equation, one has instead

$$\mathfrak{L}\chi(t) = (p + \xi_0)^{-1}. \tag{30}$$

Thus the persistent correlations can be described by replacing ξ_0 by $\xi(p)$, then inverting the Laplace transform. This is the procedure to be followed below.

In the usual theory, we have for large times

$$\langle x^2\rangle = 2Dt, \quad \langle x^4\rangle = 3\langle x^2\rangle^2 = 12D^2t^2, \tag{31}$$

where $D = T/m\xi_0$. Taking the Laplace transform, we obtain

$$\mathfrak{L}\langle x^2\rangle = 2D/p^2 = 2T/(m\xi_0 p^2), \quad \mathfrak{L}\langle x^4\rangle = 4!\,(T/m\xi_0)^2 p^{-3}. \tag{32}$$

Incorporating the persistent correlations as explained above, we find

$$\mathfrak{L}\langle x^2\rangle = 2Dp^{-2}[1 + a(p/\nu)^{1/2}]^{-1}, \quad \mathfrak{L}\langle x^4\rangle = 4!\,D^2p^{-3}[1 + a(p/\nu)^{1/2}]^{-2}. \tag{33}$$

The Laplace transform can now be inverted, and the result for long times is

$$\langle x^2\rangle = 2Dt - 4Da(t/\pi\nu)^{1/2} + \dots, \quad \langle x^4\rangle = 12D^2t^2 - 64D^2at^{3/2}(\pi\nu)^{-1/2} + \dots. \tag{34}$$

We then obtain

$$Q(t) = -16D^2at^{3/2}(\pi\nu)^{-1/2}. \tag{35}$$

Again the second-order diffusion constant D_2 is seen to be infinite.

Typical values of the parameters for Brownian motion of solid particles in air would be

$$a = 5\times 10^{-5}\text{ cm}, \quad D = 2.4\times 10^{-7}\text{ cm}^2/\text{sec}, \quad \nu = 0.14\text{ cm}^2/\text{sec}. \tag{36}$$

With these values, and for a time $t = 1$ sec, one finds $l_2 = 9.1\times 10^{-5}$ cm, while in contrast $l = 6.9\times 10^{-4}$ cm.

The distribution function $P(x, t)$ for displacement is given by the inverse Fourier transform (with respect to variable k) of the generating function (7); using expression (9), one must also invert the Laplace transform. The small-p behavior of $\overline{G}(k, p)$ governs the long-time behavior of $G(k, t)$. The divergence of D_2 indicates that $\lambda(k, p)$ cannot be expanded in k for small p, so to calculate $\overline{G}(k, p)$ we evaluate

$$\overline{G}(k, p) = [p + \lambda(k, p)]^{-1}, \tag{37}$$

with

$$\lambda(k, p) \to D_0k^2[1 - B(p + \alpha k^2)^{1/2} f(p, k)], \tag{38}$$

as follows from Eqs. (A6), (A14), (A18), and (A25) of the Appendix. Equation (38) represents the asymptotic behavior of $\lambda(k,p)$ for both small k and small p. To invert the Fourier-Laplace transform of $\overline{G}(k,p)$ we make the simplification of replacing $f(p,k)$ by its value at $p=0$, which is a constant independent of k. The transforms may then be inverted to give for long times

$$P=[4\pi(\alpha t)^{1/2}]^{-1}\int_{-\infty}^{\infty}du\, e^{-u^2} \times(e^{-(X-Y)^2}+e^{-(X+Y)^2}), \tag{39}$$

where

$$X=x/(4\alpha t)^{1/2},$$
$$Y=\frac{\lambda u^2}{t^{1/2}}\left[\left(1+\frac{D_0-\alpha}{\alpha}\frac{t}{\lambda^2u^2}\right)^{1/2}-1\right], \tag{40}$$
$$\lambda=[\tfrac{1}{2}(B'D_0)][\alpha(D_0-\alpha)]^{-1/2},$$

and $B'=Bf(0,k)$. For $B=0$ the result (39) reduces to the Gaussian,

$$P_0=(4\pi D_0t)^{-1/2}e^{-x^2/4D_0t}. \tag{41}$$

For $B\neq 0$, P is more sharply peaked than P_0, although the difference is quite small. For example, with the numerical parameters introduced above one finds that, for $x=(4D_0t)^{1/2}$, P is about 0.3% smaller than P_0, while at $x=0$, it is larger by about one part in 10^4.

For Brownian motion we begin with the Gaussian (41), which is the long-time approximation to the distribution function of the usual theory. Its Laplace transform is

$$\mathfrak{L}P_0=(4D_0p)^{-1/2}e^{-|x|(p/D_0)^{1/2}}. \tag{42}$$

Replacing ξ_0 by $\xi(p)$, we obtain

$$\mathfrak{L}P=(4D_0p)^{-1/2}[1+a(p/\nu)^{1/2}]^{1/2} \times\exp\{-|x|(p/D_0)^{1/2}[1+a(p/\nu)^{1/2}]^{1/2}\}. \tag{43}$$

To invert the Laplace transform we again consider the small-p or long-time approximation. The result is

$$P=P_0\{1+\tfrac{1}{2}(a|x|/t)(\nu D)^{-1/2} \times(x^2/4Dt)+\cdots\}. \tag{44}$$

Corrections to this result would be obtained by starting with the exact distribution function of the usual theory rather than its asymptotic form [(41)]. However, an analysis of such corrections shows that they are negligible except for very small x.

From Eq. (44), it is seen that P is more sharply peaked than P_0. However, the difference is again quite small.

We are indebted to Professor J. R. Dorfman for discussion and communication of his own calculations on this problem.

APPENDIX

To determine the eigenfunction $g(k,p,v)$ and eigenvalue $\lambda(k,p)$, Eq. (12) is written as a problem in perturbation theory:

$$(i\vec{k}\cdot\vec{v}+C)g=\lambda g, \tag{A1}$$

where $C\equiv nJ-n\mathfrak{B}$ and $i\vec{k}\cdot\vec{v}$ is taken as the perturbation. In particular, we are interested in the eigenfunction and eigenvalue obtained from the unperturbed eigenfunction 1, with eigenvalue zero:

$$C1=0. \tag{A2}$$

The corresponding adjoint equation is

$$(-i\vec{k}\cdot\vec{v}+C^\dagger)\tilde{g}=\tilde{\lambda}\tilde{g}. \tag{A3}$$

It is readily shown that $C^\dagger$ is the complex conjugate of C,

$$C^\dagger=C^*, \tag{A4}$$

where the asterisk denotes complex conjugation. Furthermore, it follows from (A4) and (A3) that

$$\tilde{g}=g^*,\quad \tilde{\lambda}=\lambda^*. \tag{A5}$$

The perturbation expansion is obtained by writing $i\vec{k}\cdot\vec{v}=ik\hat{e}\cdot\vec{v}$ (where $\hat{e}$ is a unit vector in the direction of $\vec{k}$) and

$$g=1-ikg_1+k^2g_2-ik^3g_3+\ldots,$$
$$\lambda=kX_1+k^2X_2+k^3X_3+k^4X_4+\ldots. \tag{A6}$$

The series (A6) are not expansions of g and λ in k, since C also depends on k. Rather they are expansions in the k dependence arising only from the perturbation $i\vec{k}\cdot\vec{v}$. A subsequent expansion of the coefficients in k in Eqs. (A6) will be required after the perturbation. This procedure is required since the dependence of C on k is not analytic about $k=0$ for $p\to 0$, and a perturbation expansion in the full k dependence would not converge.

Substitution of (A6) in (A1) and equating coefficients of k gives

$$X_1=X_3=0,$$
$$X_2=(\hat{e}\cdot\vec{v},g_1), \tag{A7}$$
$$X_4=(\hat{e}\cdot\vec{v},g_3),$$

and g_1, g_2, and g_3 are solutions to the equations

$$Cg_1=\hat{e}\cdot\vec{v},$$
$$Cg_2=X_2-\hat{e}\cdot\vec{v}g_1, \tag{A8}$$
$$Cg_3=X_2g_1+\hat{e}\cdot\vec{v}g_2,$$

with

$$(1,g_i)=0\,,\quad i=1,2,3\,. \tag{A9}$$

The expression for λ_4 may be simplified using (A8):

$$\begin{aligned} X_4 &= (g_3^+, \hat{e}\cdot\vec{v}) = (g_3^+, Cg_1) \\ &= (C^\dagger g_3^+, g_1)\,, \\ X_4 &= X_2(g_1^+, g_1) + (g_2^+, \hat{e}\cdot\vec{v}g_1)\,. \end{aligned} \tag{A10}$$

Also, from (A9), we have

$$\begin{aligned} (\tilde{g},g) &= 1 - k^2(g_1^+,g_1) - ik^3[(g_2^+,g_1)+(g_1^+,g_2)] \\ &\quad + k^4[(g_2^+,g_2)-(g_3^+,g_1)-(g_1^+,g_3)] + \cdots\,, \\ (\tilde{g},g) &= 1 - k^2(g_1^+,g_1) + k^4[(g_2^+,g_2) - 2(g_1^+,g_3)]\,. \end{aligned} \tag{A11}$$

Use has been made of the fact that g_1 and g_2 have opposite parity.

To estimate $(\tilde{g},g)$, X_2, and X_4, the solutions to (A8) for g_1 and g_2 will be given by the first term in a Sonine polynomial expansion:

$$\begin{aligned} g_1 &= \alpha\hat{e}\cdot\vec{v}\,, \\ g_2 &= \gamma[(\hat{e}\cdot\vec{v})^2 - (T/m)]\,. \end{aligned} \tag{A12}$$

The "constants" α and γ are determined from (A8) to be

$$\begin{aligned} \alpha &= (T/m)[(\vec{e}\cdot\vec{v}, C\vec{e}\cdot\vec{v})]^{-1}\,, \\ \gamma &= (-2\alpha T^2/m^2)\{[(\hat{e}\cdot\vec{v})^2, C(\hat{e}\cdot\vec{v})^2]\}^{-1}\,. \end{aligned} \tag{A13}$$

Then we get

$$\begin{aligned} X_2 &= (T/m)\alpha\,, \\ X_4 &= (T^2/m^2)\alpha_0^3 + (2T^2/m^2)\gamma_0\alpha_0\,, \\ (\tilde{g},g) &= 1 - k^2(T/m)\alpha^2 + k^4 2(T/m)^2 \\ &\quad\times(\gamma_0^2 - \alpha_0^4 - 2\gamma_0\alpha_0^2)\,. \end{aligned} \tag{A14}$$

Use has been made of Eqs. (A8) in obtaining the last expression. The functions α_0 and γ_0 are the $k=0$ limits of α and γ, respectively. The function α is required only to order k^2,

$$\alpha(k,p) = \alpha_0(p) + k^2\alpha_1(p) + \cdots\,, \tag{A15}$$

where α_0 and α_1 are calculated below. Compiling these results to order k^4 gives

$$\begin{aligned} \lambda(k,p) &= \lambda_2(p)k^2 + \lambda_4(p)k^4\,, \\ (\tilde{g},g) &= 1 - a(p)k^2 + b(p)k^4\,, \end{aligned} \tag{A16}$$

with

$$\begin{aligned} \lambda_2(p) &= (T/m)\alpha_0(p)\,, \\ \lambda_4(p) &= (T/m)[\alpha_1(p) + (T/m)\alpha_0(\alpha_0^2 + 2\gamma_0)]\,, \\ a(p) &= (T/m)\alpha_0^2(p)\,, \\ b(p) &= 2\left(\frac{T}{m}\right)^2\left(\frac{-m\alpha_0(p)\alpha_1(p)}{T} + [\gamma_0^2(p) - \alpha_0^4(p) - 2\gamma_0(p)\alpha_0^2(p)]\right)\,. \end{aligned} \tag{A17}$$

Direct calculation shows that $\lim_{p\to 0}\gamma_0(p)$ and $\lim_{p\to 0}\alpha_0(p)$ are finite. The most singular part of $\lambda_4(p)$ and $b(p)$ for small p therefore comes from $\alpha_1(p)$.

The behavior of $\alpha_0(p)$ and $\alpha_1(p)$ is determined from (A13),

$$\begin{aligned} \alpha(k,p) &= \frac{T}{m}[(\hat{e}\cdot\vec{v}, nJ\hat{e}\cdot\vec{v}) - (\hat{e}\cdot\vec{v}, n\mathcal{B}\hat{e}\cdot\vec{v})]^{-1} \\ &= \frac{mD_0}{T}\left(1 - \frac{m^2D_0}{T^2}(\hat{e}\cdot\vec{v}, n\mathcal{B}\hat{e}\cdot\vec{v})\right)^{-1}\,. \end{aligned} \tag{A18}$$

Here D_0 is the usual Boltzmann self-diffusion constant. The contribution from the ring operator is determined as follows:

$$(\hat{e}\cdot\vec{v}, n\mathcal{B}\hat{e}\cdot\vec{v}) = n\int_{k'<k_m}\frac{d\vec{k}'}{(2\pi)^3}\sum_{\alpha=1}^{3}\frac{M_\alpha^2(\vec{k}',\vec{k}-\vec{k}')}{[p + D(k') + p_\alpha(\vec{k}-\vec{k}')]}\,, \tag{A19}$$

with

$$\begin{aligned} M_\alpha(\vec{k}',\vec{k}-\vec{k}') &= \int d\vec{v}_1\int d\vec{v}_2\, f_0(1)f_0(2)\hat{e}\cdot\vec{v}_1 \\ &\quad\times\langle 0,0|t_{12}|0,0\rangle\,\psi_\alpha(v_2,\vec{k}-\vec{k}')\phi(v_1,\vec{k}')\,. \end{aligned} \tag{A20}$$

Here ψ_α and ϕ are the hydrodynamic eigenfunctions of the linearized Boltzmann and Boltzmann-Lorentz operators, respectively:

$$\begin{aligned} (i\vec{k}'\cdot\vec{v}_1 + nJ_1)\phi(\vec{v}_1,\vec{k}') &= D(k')\phi(v_1,k')\,, \\ [i(\vec{k}-\vec{k}')\cdot\vec{v}_2 + nI_2]\psi_\alpha(\vec{v}_2,\vec{k}-\vec{k}') &= p_\alpha(\vec{k}-\vec{k}')\psi_\alpha(\vec{v}_2,\vec{k}-\vec{k}')\,. \end{aligned}$$

The sum over α in (A19) excludes the two sound modes since they do not contribute to the long-time behavior. Denoting the two shear modes by ψ_1 and ψ_2, and the thermal diffusion mode by ψ_3, these eigenfunctions have the general form for small $\vec{k}'$, $\vec{k}-\vec{k}'$,

$$\begin{aligned} \psi_1(\vec{v}_2,\vec{k}-\vec{k}') &= \hat{e}_i^{(1)}(k-k')(m/T)^{1/2}v_{2,i} + (k-k')_i C_{1,i}(v_2,\vec{k}-\vec{k}')\,, \\ \psi_2(\vec{v}_2,\vec{k}=\vec{k}') &= \hat{e}_i^{(2)}(k-k')(m/T)^{1/2}v_{2,i} + (k-k')_i C_{2,i}(v_2,\vec{k}-\vec{k}')\,, \\ \psi_3(\vec{v}_2,\vec{k}-\vec{k}') &= (1/T)(\tfrac{2}{5})^{1/2}(\tfrac{1}{2}mv^2 - \tfrac{5}{2}T) + (\vec{k}-\vec{k}')_i C_{3,i}(v_2,\vec{k}-\vec{k}')\,, \\ \phi(\vec{v}_1,\vec{k}') &= 1 + k_1'\cdot A_i(v_2,\vec{k}')\,, \end{aligned} \tag{A21}$$

where $\hat{e}_i^{(1)}(\vec{k}-\vec{k}')$ and $\hat{e}_i^{(2)}(\vec{k}-\vec{k}')$ are mutually orthogonal unit vectors, orthogonal to $\vec{k}-\vec{k}'$. Substitution of (A21) into (A20), using the fact that

$$(v_i, C_{\alpha,j}) = 0\,, \quad \alpha = 1,2,3$$

$$n\int d\vec{v}_2 f_0(2)\langle 0,0\,|\,t_{12}\,|\,0,0\rangle v_{1,i} \approx (T/D_0 m) v_{1,i}\,,$$

yields

$$M_1^2(\vec{k}',\vec{k}-\vec{k}') + M_2^2(\vec{k}',\vec{k}-\vec{k}') = \left(\frac{T}{m}\right)^3 \frac{1}{(nD_0)^2}\left[1-\left(\frac{\hat{e}\cdot(\vec{k}-\vec{k}')}{|\vec{k}-\vec{k}'|}\right)^2 + k'\Delta_1(\vec{k}',\vec{k}-\vec{k}')\right],$$

$$M_3(\vec{k}',\vec{k}-\vec{k}') = k'\Delta_2(\vec{k}',\vec{k}-\vec{k}')\,. \qquad \text{(A22)}$$

The functions $\Delta_1(\vec{k}',\vec{k}-\vec{k}')$ and $\Delta_2(\vec{k}',\vec{k}-\vec{k}')$ are analytic functions of k' and $|k-k'|$ (but not of k and k') whose explicit form will not be required. The fact that they are multiplied by a factor of k' implies their contribution to the integral in (A19) is less singular for small p than the other terms in (A22), and hence does not contribute to the long-time behavior. To see this, note that

$$\Delta_1(\vec{k}',\vec{k}-\vec{k}') = \Delta_1'(k', k/k') = c_0(k') + c_1(k')(k/k') + c_2(k/k')^2 + \ldots\,,$$

where the $c_i(k')$ are analytic in k'. The first equation of (A22) is then, to order k^2,

$$M_1^2(\vec{k}',\vec{k}-\vec{k}') + M_2^2(\vec{k}',\vec{k}-\vec{k}') = \left(\frac{T}{m}\right)^3\frac{1}{(nD_0)^2}\{[(1-x^2)+k'c_0(k')] + [(1-x^2)2x + k'c_1(k')]k/k' + [(1-x^2)(4x^2-1)+k'c_2(k')](k/k')^2+\ldots\}\,, \qquad \text{(A23)}$$

where $x = \vec{k}\cdot\vec{k}'/kk'$. A change of variables in (A19), $k' \to (p)^{1/2}k'$, shows that the contributions from c_i in (A23) are less singular for small p by a factor of $(p)^{1/2}$. The functions Δ_1 and Δ_2 are thus not required for the long-time behavior here. For similar reasons we can replace

$$D(k') \to D_0 k'^2\,,$$

$$p_1(k-k') = p_2(k-k') \to \nu(\vec{k}-\vec{k}')^2\,.$$

Then to order k^2, we need only

$$(\hat{e}\cdot\vec{v}, n\mathcal{B}\hat{e}\cdot\vec{v}) \to \left(\frac{T}{m}\right)^3\frac{1}{nD_0^2}\int_{k'<k_m} d\vec{k}'\left[1-\left(\frac{\hat{e}\cdot(\vec{k}-\vec{k}')}{|k-k'|}\right)^2\right][p + D_0k'^2 + \nu(\vec{k}-\vec{k}')^2]^{-1}\,. \qquad \text{(A24)}$$

This integral gives the correct behavior for small k and p, and it is instructive to give it explicitly before performing the expansion to order k^2:

$$(\hat{e}\cdot\vec{v}, n\mathcal{B}\hat{e}\cdot\vec{v}) \to \frac{T^3k_m}{m^3D_0^2(D_0+\nu)} - \frac{T^3(p+\alpha k^2)^{1/2}}{6\pi m^3D_0^2 n(D_0+\nu)^{3/2}} f(p,k)\,, \qquad \text{(A25)}$$

$$f(p,k) \equiv \frac{3}{8}\left[1 - \frac{\alpha k}{\nu(p+\alpha k^2)^{1/2}} + \left(\frac{(z+D_0k^2)\alpha\nu}{D_0k^2}\right) \times \frac{\alpha k}{\nu(p+\alpha k^2)^{1/2}}\tan^{-1}\frac{\alpha k}{\nu(p+\alpha k^2)^{1/2}}\right],$$

where $\alpha \equiv D_0\nu/(D_0+\nu)$. The nonanalytic dependence on p and k about $p=0$, $k=0$ is the source of the divergence of D_2. To order k^2, Eqs. (A25) give

$$(\hat{e}\cdot\vec{v}, n\mathcal{B}\hat{e}\cdot\vec{v}) \to \frac{-T^2B}{m^2D_0}p^{1/2} - k^2\frac{T^2B(\nu+2D_0/5)}{2m^2(D_0+\nu)}p^{-1/2}\,, \qquad \text{(A26)}$$

where B is defined in Eq. (16). Use of (A26) in (A16)–(A18) give the results used in the text.

The dependence on the cutoff wave vector k_m has been neglected in (A26). The origin of k_m is due to the approximations involved in obtaining the low-density ring operator and to consideration of the contributions from hydrodynamic modes. For sufficiently large k the hydrodynamic-mode analysis breaks down. This occurs for k' of the order of the inverse mean free path. If k_m is taken to be of the order of the inverse mean free path, then $k_m \sim$ density, and should be neglected in the low-density limit.

*Research supported by the National Science Foundation.

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