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Diffusion in shear flow

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Diffusion of a tagged particle in a fluid with uniform shear flow is described. An expression for the diffusion tensor is obtained in a form similar to the Green-Kubo result for the equilibrium self-diffusion coefficient, but which is applicable even far from equilibrium. In one form the diffusion tensor is determined from a type of Einstein relationship to the nonequilibrium mean-square displacement in the Lagrangian frame for the fluid. Alternatively, the diffusion tensor is expressed as a time integral of the autocorrelation function for the velocity of the tagged particle in a local rest frame. A frequency- and shear-rate-dependent diffusion tensor is defined from these results and evaluated in two limits. The first case is the Boltzmann limit for a low-density gas, and the diffusion tensor is found to be an analytic function of both frequency and shear rate. Consequently, nonlinear transport coefficients of arbitrary order are well defined and finite. In the second case the mode-coupling contributions for a general fluid are obtained by an extension of the equilibrium mode-coupling phenomenology to shear flow. The hydrodynamic modes are obtained as a function of time and shear rate and lead to a nonanalytic dependence of the diffusion tensor on both frequency and shear rate. A universal function is obtained to describe the crossover from asymptotic frequency to asymptotic shear-rate dependence. This function is compared with a similar result predicted by a phenomenological model from nonlinear continuum mechanics.

I. INTRODUCTION

Attempts to extend the time correlation function method of linear response[1] to describe nonlinear transport in systems far from equilibrium have been limited primarily to formal analyses.[2–6] An exception is the particularly simple state of uniform shear flow in a fluid. For small values of the shear rate, the pressure tensor is linear in the shear rate (Newton's viscosity law), and the proportionality constant is the shear viscosity given by the Green-Kubo time correlation function expression. For larger shear rates the pressure tensor can be represented by a formal Taylor series expansion in powers of the shear rate, whose coefficients are the nonlinear transport coefficients.[5–7] However, in a pioneering study of this problem Kawasaki and Gunton showed that mode-coupling effects lead to a nonanalytic dependence of the pressure tensor on the shear rate,[8,9] and consequently some or all of the nonlinear coefficients in the Taylor series are divergent.[10] More recently, methods have been developed for computer simulation of transport in nonequilibrium states,[11–15] and the qualitative results seem to be consistent with the nonanalytic form predicted by Kawasaki and Gunton.[16] One of the objects of interest in both the theoretical and computer studies is the shear viscosity η. At zero shear rate, η is given by the low-frequency limit of the Fourier transform of the Green-Kubo time correlation function. Mode-coupling effects are responsible for a square-root dependence on the frequency (long-time tails),

$$\eta(0,w)\rightarrow\eta_0-\eta'\sqrt{w} \quad \text{for small } w\ . \tag{1.1}$$

At zero frequency, the mode-coupling results of Kawasaki and Gunton lead to a square-root dependence on the shear rate,

$$\eta(a,0)\rightarrow\eta_0-\eta''\sqrt{a} \quad \text{for small } a\ . \tag{1.2}$$

Thus if a frequency- and shear-rate-dependent viscosity is defined, $\eta(a,w)$, it is predicted to be nonanalytic in both the frequency and shear rate. The nonequilibrium computer simulations can be fit with the forms (1.1) and (1.2), but the coefficients η' and η'' obtained are an order of magnitude different from those of mode-coupling theory. The reason for this discrepancy is not understood at present, but some of the points at issue have been reviewed at a recent conference on this subject.[17] The fact that both nonanalyticities arise theoretically from mode coupling suggests a relationship of the two, even though the physical phenomena in Eqs. (1.1) and (1.2) are quite different (viscoelasticity in the former, non-Newtonian flow in the latter). There have been no mode-coupling calculations of $\eta(a,w)$ at both finite frequency and shear rate, so that such a relationship is at present obscure. However, Zwanzig has noted that the phenomenological Goddard-Miller rheological equation of state leads to a definite connection between the frequency and shear-rate dependence.[18] In particular it would imply that the coefficients η' and η'' in Eqs. (1.1) and (1.2) are equal. The results of the computer simulations leave this possibility open, but mode-coupling theory leads to an order of magnitude difference between η' and η'' (in three dimensions). The validity of the Goddard-Miller model in this context is therefore appealing but uncertain.

The objective here is to describe a related nonlinear transport process, that of self-diffusion in shear flow. Self-diffusion involves only single-particle motion and is therefore somewhat simpler to treat theoretically. It is also a process that can be investigated by the current methods for nonequilibrium computer simulation.[19]

There are two main components to the results presented here. The first is the derivation of a general expression for the diffusion tensor that is applicable to the nonequilibrium state of uniform shear flow. The result generalizes the corresponding Green-Kubo equilibrium time correlation function expression to states far from equilibrium and provides the appropriate object for both theoretical investigation and computer simulation. The second component is the evaluation of this result for the diffusion tensor in two different limiting cases, to determine its frequency and shear-rate dependence.

In Sec. II the continuity equation for the probability density describing the position of the tagged particle is considered. The current density in this equation consists of two parts, one due to convection at the local velocity of the fluid and a remainder due to irreversible transport. The diffusion tensor is identified by expanding the irreversible part of the probability current to first order in the gradient of the probability density, but with no restriction on the shear rate. Some comments on the distinction between the "molecular" diffusion tensor and the Taylor diffusion tensor (due purely to convection by a nonuniform flow field[20]) are given. The diffusion tensor is expressed as the time integral of a nonequilibrium autocorrelation function for the velocity of the tagged particle in its local fluid rest frame, generalizing the Green-Kubo expression to the nonequilibrium state. This result can also be expressed as an Einstein relation in terms of the mean-square displacement of the particle in the Lagrangian frame of the fluid.

The diffusion tensor is evaluated in Sec. III from results obtained previously for the velocity autocorrelation function that are exact for Maxwell molecules in the Boltzmann limit.[21] The effects of viscous heating are included and the dependence on frequency and shear rate is displayed explicitly. As expected, in this limit the diffusion tensor is analytic in all variables. Next, the mode-coupling contributions to the frequency- and shear-rate-dependent diffusion tensor are calculated. For small shear rate and frequency, the diffusion tensor is found to have the form

$$D_{ij}(a,w)\rightarrow D_0[\delta_{ij}-C\sqrt{w}\,\Delta_{ij}(a/w)]\ , \tag{1.3}$$

where C is a constant. The asymptotic form of $\Delta_{ij}(x)$ is $\sqrt{x}$ for large x, and constant for small x. Consequently $D_{ij}(a,w)$ exhibits both of the expected nonanalyticities analogous to Eq. (1.1). The function $\Delta_{ij}(x)$ is independent of any fluid parameters or state condition and is therefore universal for all fluids governed by the Navier-Stokes equations. It describes the crossover from asymptotic frequency dependence to asymptotic shear rate dominated behavior. This result is compared to the predictions of the Goddard-Miller model. A preliminary report of these results has been given elsewhere.[22]

II. DIFFUSION TENSOR

A fluid of mechanically identical particles is taken to be in a nonequilibrium state of uniform shear flow. The flow velocity has the form

$$v_i(\vec{r})=a_{ij}r_j\ , \tag{2.1}$$

where $\vec{r}$ is an arbitrary field point in the fluid and a_{ij} is a constant tensor with the properties (the Einstein summation convention is used here and below)

$$a_{ii}=0=a_{ik}a_{kj}=a_{ki}a_{jk},\quad a\equiv\sqrt{a_{ij}a_{ij}}\ . \tag{2.2}$$

In addition, the density, pressure, heat flux, and pressure tensor are spatially uniform. It is easily verified that the macroscopic conservation laws under these conditions degenerate to[23]

$$\frac{\partial}{\partial t}n(t)=0,\quad \frac{\partial}{\partial t}u(t)=-a_{ij}P_{ij}(t)\ , \tag{2.3}$$

where $n(t)$ is the number density and $u(t)$ is the internal-energy density. Consequently, the conditions of uniform shear flow are compatible with the macroscopic conservation laws if the density is strictly constant and the energy (or temperature) increases due to the shear rate. Equation (2.3) must be supplemented with an explicit form for the pressure tensor $P_{ij}(t)$ as a function of the shear rate.

Let the position and velocity of one of the particles be identified by $\vec{R}(t)$ and $\vec{U}(t)$, respectively. The remaining degrees of freedom of the fluid are denoted by the phase point Γ. For uniform shear flow the initial state of the fluid is assumed to be represented by the distribution function

$$\rho(t=0)=\rho(\vec{U}',\Gamma;0)\ , \tag{2.4}$$

where $\vec{U}'$ is the velocity of the tagged particle in the local rest frame of the fluid

$$U_i'\equiv U_i(0)-v_i(\vec{R}(0))\ . \tag{2.5}$$

The time evolution is given by the Liouville equation with boundary conditions appropriate for uniform shear flow. The particular choice (2.4) depends on $\vec{R}$ only through the relative velocity and will be referred to as the uniform state. Next, imagine that the tagged particle is observed to be at the point $\vec{r}_0$ at $t=0$. Instead of (2.4) the initial state is represented in this case by

$$\rho(t=0)=\Omega\delta(\vec{R}(0)-\vec{r}_0)\rho(\vec{U}',\Gamma;0)\ , \tag{2.6}$$

where the volume factor Ω is required for normalization.

The probability density to find the tagged particle at any point $\vec{r}$ at a later time t given that it was at $\vec{r}_0$ initially is defined by

$$P(\vec{r};t)=\langle\delta(\vec{R}(t)-\vec{r})\rangle_{\vec{r}_0}\ . \tag{2.7}$$

The brackets $\langle\ \rangle_{\vec{r}_0}$ denote an ensemble average over the initial state (2.6). Conservation of probability is expressed by the continuity equation

$$\begin{gathered}\frac{\partial}{\partial t}P(\vec{r};t)+\vec{\nabla}\cdot\vec{J}(\vec{r};t)=0\ ,\\ \vec{J}(\vec{r};t)\equiv\langle\vec{U}(t)\delta(\vec{R}(t)-\vec{r})\rangle_{\vec{r}_0}\ .\end{gathered} \tag{2.8}$$

Equations (2.8) follow directly from (2.7) by differentiation with respect to time. The current $\vec{J}(\vec{r};t)$ may be divided into a contribution due to pure convection by the macroscopic fluid flow field and a remaining dissipative part $\vec{J}^*(\vec{r};t)$:

$$\vec{J}(\vec{r};t)=\vec{v}(\vec{r})P(\vec{r};t)+\vec{J}^*(\vec{r};t)\ ,$$
$$\vec{J}^*(\vec{r};t)=\langle \vec{U}'(t)\delta(\vec{R}(t)-\vec{r})\rangle_{\vec{r}_0}\ . \tag{2.9}$$

The continuity equation then takes the form

$$\left[\frac{\partial}{\partial t}+\vec{v}(\vec{r})\cdot\vec{\nabla}\right]P(\vec{r};t)+\vec{\nabla}\cdot\vec{J}^*(\vec{r};t)=0\ . \tag{2.10}$$

In this form the changes in $P(\vec{r};t)$ due to convection have been made explicit, so the *molecular* diffusion process can be identified with the irreversible part of the current $\vec{J}^*(\vec{r};t)$. The diffusion limit is defined by

$$J_i^*(\vec{r};t)\rightarrow -D_{ij}(a;t)\frac{\partial}{\partial r_j}P(\vec{r};t) \tag{2.11}$$

and is expected to apply for sufficiently long times and small gradients. The diffusion tensor is taken to be independent of $\vec{r}$, since the flow is uniform, but depends on the shear rate a_{ij} and time (due to viscous heating). It turns out that the convective part of the current can also be represented as a diffusion process because of the space dependence of the velocity field. This is called Taylor diffusion[20] and is discussed briefly at the end of this section.

To identify the diffusion tensor in terms of the molecular properties of the system, it is convenient to transform the continuity equation (2.10) to the Lagrangian coordinates of the fluid,

$$q_i=r_i-v_i(\vec{r})t\equiv\Lambda_{ij}(t)r_j\ , \tag{2.12}$$

where the tensor $\Lambda_{ij}(t)$ is the relative deformation gradient for uniform shear flow[24]

$$\Lambda_{ij}(t)=\delta_{ij}-a_{ij}t\ ,$$
$$[\underline{\Lambda}^{-1}(t)]_{ij}=\Lambda_{ij}(-t)\ . \tag{2.13}$$

The second equality in (2.13) follows directly from the properties of a_{ij}, Eq. (2.2). Application of the transformation (2.12) to the continuity equation (2.10) then gives

$$\frac{\partial}{\partial t}P'(\vec{q};t)+\frac{\partial}{\partial q_i}J_i^{*\prime}(\vec{q};t)=0 \tag{2.14}$$

with

$$P'(\vec{q};t)\equiv P(\underline{\Lambda}^{-1}\vec{q};t)\ ,$$
$$J_i^{*\prime}(\vec{q};t)=\Lambda_{ij}(t)J_j^*(\underline{\Lambda}^{-1}\vec{q};t)\ . \tag{2.15}$$

The motivation for this transformation is to remove the effects of pure convection so that $P'(\vec{q};t)$ changes only due to the dissipative part of the current.

From the definition (2.7), $P'(\vec{q};t)$ can be identified as

$$P'(\vec{q};t)=\langle\delta(\vec{R}(t)-\underline{\Lambda}^{-1}\vec{q})\rangle_{\vec{r}_0}$$
$$=\langle\delta(\vec{Q}(t)-\vec{q})\rangle_{\vec{r}_0}\ , \tag{2.16}$$

where $\vec{Q}(t)$ is the particle's position in the Lagrangian coordinate system for the fluid

$$Q_i(t)\equiv\Lambda_{ij}(t)R_j(t)\ . \tag{2.17}$$

The second equality in (2.16) follows from the fact that the Jacobian of the transformation (2.12) equals one. Next, taking explicit account of the initial state (2.6), $P'(q,t)$ may be expressed in terms of the displacement of this new position variable,

$$P'(\vec{q};t)=\langle\delta(\vec{Q}(t)-\vec{Q}(0)-(\vec{q}-\vec{r}_0))\rangle_{\vec{r}_0}\ . \tag{2.18}$$

It is shown in Appendix A that $P'(\vec{q};t)$ is translationally invariant, i.e., $P'(\vec{q};t)$ depends on $\vec{q}$ and $\vec{r}_0$ only through their difference $\vec{q}-\vec{r}_0$. This property does not hold for the probability density $P(\vec{r};t)$ in the laboratory coordinates where the symmetry is broken by the convective flow. As a consequence of this invariance, $P'(\vec{q};t)$ can be reduced to an average over the uniform ensemble

$$P'(\vec{q};t)=\langle\delta(\vec{Q}(t)-\vec{Q}(0)-(\vec{q}-\vec{r}_0));0\rangle\ , \tag{2.19}$$

where the brackets $\langle\ ;0\rangle$ now denote the average over the initial uniform ensemble given by (2.4). This is a significant result because it implies that the tagged-particle dynamics is determined from the same nonequilibrium state as that which characterizes the hydrodynamic variables of uniform shear flow for the fluid.

The diffusion limit for $P'(\vec{q};t)$ is most easily extracted using a Fourier representation:

$$P'(\vec{q};t)=\int\frac{d\vec{k}}{(2\pi)^3}e^{-i\vec{k}\cdot(\vec{q}-\vec{r}_0)}e^{C(\vec{k};t)}\ ,$$
$$C(\vec{k};t)\equiv\ln\langle e^{i\vec{k}\cdot[\vec{Q}(t)-\vec{Q}(0)]};0\rangle\ . \tag{2.20}$$

Differentiating with respect to time then gives

$$\frac{\partial}{\partial t}P'(\vec{q};t)=\int\frac{d\vec{k}}{(2\pi)^3}e^{-i\vec{k}\cdot(\vec{q}-\vec{r}_0)}$$
$$\times\left[\frac{\partial}{\partial t}C(\vec{k};t)\right]e^{C(\vec{k};t)}\ . \tag{2.21}$$

An expansion of $\partial C(\vec{k};t)/\partial t$ in powers of $\vec{k}$ generates a gradient expansion in $P'(\vec{q};t)$. Retaining only terms to second order[25] for the diffusion limit gives Eq. (2.14) with

$$J_i^{*\prime}(\vec{q};t)=-D'_{ij}(a;t)\frac{\partial}{\partial q_j}P'(\vec{q};t)\ ,$$
$$D'_{ij}(a;t)=\frac{1}{2}\frac{\partial}{\partial t}\langle[Q_i(t)-Q_i(0)][Q_j(t)-Q_j(0)];0\rangle\ . \tag{2.22}$$

To obtain (2.21) use has been made of

$$\langle U_i'(t);0\rangle=0\ , \tag{2.23}$$

i.e., the average velocity of each particle is that of the fluid at the position of the particle.

The diffusion tensor in the laboratory frame is now easily obtained by inverting (2.15) to give

$$J_i^*(\vec{r};t)=-D_{ij}(a;t)\frac{\partial}{\partial r_j}P(\vec{r};t)\ ,$$
$$D_{ij}(a;t)=\Lambda_{ik}(-t)\Lambda_{jl}(-t)D'_{kl}(a;t)\ . \tag{2.24}$$

This is the desired result. The diffusion tensor defined by (2.24) can be related to the velocity autocorrelation function using the identity

$$Q_i(t)-Q_i(0)=\int_0^t d\tau\,\Lambda_{ij}(\tau)U'_j(\tau) \tag{2.25}$$

as follows from the definition of $\vec{Q}(t)$. Substitution of (2.25) and (2.22) into (2.24) gives the diffusion tensor as

$$D_{ij}(a;t)=\int_0^t d\tau\,\Lambda_{jk}(\tau-t)\langle U'_i(t)U'_k(\tau);0\rangle\ , \tag{2.26}$$

where it has been recognized that only the symmetric part of $D_{ij}(a;t)$ contributes to $\vec{\nabla}\cdot\vec{J}^*$. This result is similar to the Green-Kubo expression for self-diffusion in an equilibrium fluid. The differences here are the nonequilibrium average $\langle\ ;0\rangle$ representing shear flow instead of an equilibrium average, the appearance of the *relative* velocity (local Gallilean transformation), and the transformation matrix Λ_{ij}. A second representation for the diffusion tensor can be obtained in a form similar to an Einstein relation. Direct substitution of (2.22) into (2.24) and use of the definition of $\vec{Q}(t)$ gives

$$D_{ij}(a;t)=\Lambda_{ik}(-t)\Lambda_{jl}(-t)\frac{1}{2}\frac{\partial}{\partial t}$$
$$\times\langle[(R_k(t)-R_k(0)-v_k(\vec{R}(t))t]$$
$$\times[R_l(t)-R_l(0)-v_l(\vec{R}(t))t];0\rangle\ . \tag{2.27}$$

Consequently Eq. (2.27) involves the mean-square displacement of the particle relative to the convected position of the fluid element occupied at time t.

The subtraction of effects due simply to the motion of the fluid characterizes $D_{ij}(a;t)$ as the molecular diffusion tensor. This is in contrast to what is sometimes referred to as the Taylor diffusion coefficient. The latter is due entirely to the convective part of the flux $\vec{J}(\vec{r};t)$ in Eq. (2.9) and arises because convection by a *nonuniform* flow field can be represented by a diffusion equation with an effective diffusion tensor.[20,26] To emphasize this difference in the present context, consider the special case of a particle placed initially at $\vec{r}_0=\vec{0}$, symmetrically in the flow field. Then it is possible to show, by direct solution of the diffusion equation, the equivalence of convection and an effective diffusion,

$$\vec{v}(\vec{r})\cdot\vec{\nabla}P(\vec{r};t)=[D_{ij}(a;t)-\bar{D}_{ij}(a;t)]\frac{\partial^2}{\partial r_i\,\partial r_j}P(\vec{r};t) \tag{2.28}$$

with $D_{ij}(a;t)$ given as above and

$$\bar{D}_{ij}(a;t)=\int_0^t d\tau\langle U_i(t)U_j(\tau)\rangle_{\vec{r}_0}\ . \tag{2.29}$$

The diffusion equation for $P(\vec{r};t)$ is, with Eq. (2.11),

$$\frac{\partial}{\partial t}P(\vec{r};t)-\bar{D}_{ij}(a;t)\frac{\partial^2}{\partial r_i\,\partial r_j}P(\vec{r};t)=0\ , \tag{2.30}$$

where the convective term of Eq. (2.10) no longer appears. The diffusion tensor $\bar{D}_{ij}$ is defined in terms of the velocity autocorrelation function in the laboratory frame, in contrast to the definition of D_{ij}, Eq. (2.26). Consequently, $\bar{D}_{ij}$ represents *both* the diffusion within a fluid element due to molecular motion *and* an effective diffusion due to nonuniform convection. This distinction is important because the velocity autocorrelation function in (2.29) has a qualitatively different time dependence from that in the local rest frame.[21] The diffusion tensor $\bar{D}_{ij}(a;t)$ is expected to grow without bound in time,[27] whereas the molecular diffusion coefficient is expected to approach a finite limiting value (see Sec. III). The divergent part of $\bar{D}_{ij}(a;t)$ therefore results from the choice to represent convection as diffusion, rather than from any fundamental breakdown of the diffusion process; the diffusion equation (2.10), with (2.11) and a finite D_{ij}, applies even when $\bar{D}_{ij}(a;t)$ is not well defined.[28]

The molecular diffusion coefficient still has some dependence on the convective flow field, of course, and some of this can be extracted more explicitly. The time dependence of the velocity autocorrelation function in (2.26) is determined from the equations of motion

$$\frac{d}{dt}U'_i+a_{ij}U'_j=\Lambda_{ij}F_j\ , \tag{2.31}$$

where $\vec{F}$ is the force on the tagged particle. The term $a_{ij}U'_j$ is an inertial force due to the inhomogeneous flow field. This inertial term may be eliminated by the introduction of a new "velocity" $\vec{V}(t)$,

$$V_i(t)=\Lambda_{ij}(-t)U'_j(t),\quad \frac{d}{dt}\vec{V}=\vec{F}\ . \tag{2.32}$$

Thus $\vec{V}$ obeys Newton's equations for an inertial frame, but still is a measure of motion relative to the local (noninertial) rest frame. With this new velocity variable, Eq. (2.26) may be written

$$D_{ij}(a;t)=\int_0^t d\tau[\underline{\Lambda}(t-\tau)\underline{G}(t,\tau)\underline{\Lambda}^T(\tau-t)]_{ij}\ , \tag{2.33}$$

where $\underline{\Lambda}^T(t)$ is the transpose of $\underline{\Lambda}(t)$ and

$$G_{ij}(t,\tau)\equiv\langle V_i(t-\tau)V_j(0);\tau\rangle\ . \tag{2.34}$$

For purposes of analysis in the next sections it is convenient to define a dimensionless frequency- and shear-rate-dependent diffusion tensor

$$\widetilde{D}^*_{ij}(a;w)\equiv-\mathrm{Re}(iw)\int_0^\infty dt\,e^{iwt}D^*_{ij}(a;t)\ , \tag{2.35}$$

where

$$D^*_{ij}(a;t)\equiv D_{ij}(a;t)/D(T(t)) \tag{2.36}$$

and $D(T(t))$ is the equilibrium diffusion coefficient as a function of the nonequilibrium temperature. The notation Re in (2.35) indicates that the real part is to be taken. In equilibrium Eq. (2.35) is proportional to the Fourier transform of the velocity autocorrelation function. More generally, it is straightforward to show that

$$\lim_{w\to 0} \tilde{D}^*_{ij}(a;w) = \lim_{t\to\infty} D^*_{ij}(a;t) \tag{2.37}$$

whenever both of these limits exist.

III. BOLTZMANN LIMIT

To illustrate the differences to be expected between the diffusion coefficient for equilibrium and that for shear flow, a low-density gas in the Boltzmann limit is considered here. The calculation of fluctuations in shear flow for this case has been discussed elsewhere for the special example of Maxwell molecules.[21] For this potential model all of the properties of the fluid and tagged particle can be calculated exactly. In particular, the rest-frame velocity autocorrelation function was determined to be

$$\langle U_i'(t)U_j'(\tau);0\rangle = e^{-\nu_1(t-\tau)}\Lambda_{ij}(t-\tau)\langle U_k'(\tau)U_j'(\tau);0\rangle\ , \tag{3.1}$$

where ν_1 is one of the eigenvalues of the Boltzmann operator and depends only on the mass and potential parameters. The diffusion tensor is then in the form of Eq. (2.33), with

$$G_{ij}(t,\tau) = e^{-\nu_1(t-\tau)}\langle U_i'(\tau)U_j'(\tau);0\rangle\ . \tag{3.2}$$

The equal-time correlation function is simply related to the macroscopic pressure tensor by

$$\langle U_i'(\tau)U_j'(\tau);0\rangle = P_{ij}(\tau)/\rho\ , \tag{3.3}$$

where ρ is the mass density.

The nonstationarity of the uniform shear flow is reflected through the time dependence of the pressure tensor $P_{kl}(\tau)$ and is due to viscous heating. Again for the special case of Maxwell molecules, $P_{kl}(\tau)$ can be calculated exactly from the nonlinear Boltzmann equation. The asymptotic form of the pressure tensor and temperature, $T(t)$, for $\nu_1 t \gg 1$ is found to be[21]

$$\begin{aligned} &P_{ij}(t) \to C_{ij}(a)e^{z_1(a)t}\ ,\\ &T(t) \to C(a)e^{z_1(a)t}\ . \end{aligned} \tag{3.4}$$

Here C, C_{ij}, and z_1 are time-independent functions of the shear rate. Since the relevant times contributing to the integrand in (3.3) for $\nu_1 t \gg 1$ are $\nu_1\tau \gg 1$, the asymptotic forms (3.4) may be used to evaluate $D^*_{ij}(a;t)$ in Eq. (2.36) as

$$\begin{aligned} &D^*_{ij}(a;t) = \nu_1 \int_0^t d\tau[\underline{\Lambda}(t-\tau)\underline{G}^*(t,\tau)\underline{\Lambda}^T(\tau-t)]_{ij}\ ,\\ &G^*_{ij}(t,\tau) = e^{-\nu_1(t-\tau)}(nC_{ij}/\rho C)\ . \end{aligned} \tag{3.5}$$

The time integral in (3.5) is readily performed and shows an exponentially fast approach to its asymptotic value.

The frequency- and shear-rate-dependent tensor is defined by Eq. (2.35). To simplify the discussion, only the scalar trace of $\tilde{D}^*_{ij}(w,a)$ will be considered:

$$D_T(a;w) \equiv \tfrac{1}{3}\tilde{D}^*_{ii}(a;w)\ . \tag{3.6}$$

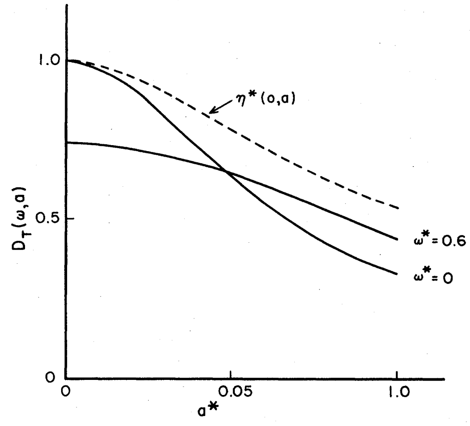

FIG. 1. $D_T(w,a)$, Eq. (3.8), as a function of reduced shear rate $a^* = a/\nu_1$ for $w^* = w/\nu_1 = 0$ and 0.6. Also shown is the reduced shear viscosity for comparison.

It is straightforward now to calculate $D_T(a;w)$ from the results in Appendix A of Ref. 21. The calculation is somewhat lengthy so only the result will be given:

$$D_T(a;w) = \frac{x}{x^2+(w^*)^2}\left[1 - \frac{c^2\lambda(1+\lambda)[x^2-3(w^*)^2]}{[x^2+(w^*)^2]^2}\right]\ , \tag{3.7}$$

$$x \equiv 1 + c\lambda,\quad c = 1.55\ .$$

The function $\lambda(a^*)$ is defined by

$$\lambda(a^*) \equiv \tfrac{4}{3}\sinh^2\{\tfrac{1}{6}\cosh^{-1}[1+9(a^*)^2]\}\ . \tag{3.8}$$

Here $a^* \equiv a/\nu_3$, $w^* \equiv w/\nu_1$. Figure 1 shows $D_T(a;w)$ as a function of shear rate. For comparison, the shear-rate-dependent viscosity $\eta^*(a) \equiv \eta(a;t)/\eta_0(T(t))$ is also shown. The shear rate dependence of $D_T(a;0)$ is seen to be similar to the non-Newtonian "shear thinning" of the viscosity. This dependence also persists at finite frequencies.

It is clear from the expression (3.7) that $D_T(a;w)$ is analytic in both w and a for the Boltzmann limit,

$$\begin{aligned} D_T(a;w) &\to 1 - \tfrac{2}{3}c(1+c)(a^*)^2 - (w^*)^2\\ &\sim 1 - \nu_1^{-2}(w^2 + 1.1a^2)\ . \end{aligned} \tag{3.9}$$

The asymptotic dependence of $D_T(a;w)$ on w and a is seen to be the same with coefficients of the same order of magnitude. However, in contrast to the Goddard-Miller model described in Sec. V, there appears to be no fundamental relationship between the origin of the frequency dependence and that of the shear rate dependence.

IV. MODE-COUPLING LIMIT

The set of local conserved densities are the phase functions whose averages obey the hydrodynamic equations, for long times. Consequently, these quantities are commonly referred to as the "slow" variables for the system. In general, the time correlation functions for transport coefficients involve other phase functions (the conserved currents) that are orthogonal to the conserved densities, so it might be expected that they reflect only the shorter, nonhydrodynamic time dependence. However, it is reasonable to expect that if the conserved densities have a slow or long-time hydrodynamic behavior, then so should their products. Since the currents in the time correlation function expressions for the transport coefficients are in general *not* orthogonal to products of the slow variables, there should be a slowly decaying hydrodynamic component that dominates for long times. This component will be referred to as the mode-coupling limit, since it arises from products of hydrodynamic modes. The analysis of the diffusion coefficient here will be limited to the lowest-order (two-mode) approximation, which provides the asymptotic long-time behavior. There are many equivalent methods to calculate the mode-coupling contributions for equilibrium time correlation functions.[29] The following discussion is therefore kept brief, to indicate only the natural extension of the equilibrium calculations to the nonequilibrium case of interest here.

To simplify the analysis it will be assumed that the appropriate macroscopic hydrodynamic equations are those for an incompressible fluid. The relevant conserved densities are

$$\hat{P}(\vec{r})\equiv\delta(\vec{r}-\vec{R}(t))\ ,$$
$$\hat{\vec{u}}(\vec{r})\equiv\rho^{-1}\sum_{\alpha=1}^{N}[\vec{p}_\alpha-m\vec{v}(\vec{r})]\delta(\vec{r}-\vec{q}_\alpha)\ , \tag{4.1}$$

where ρ is the average mass density. The caret on the variables $\hat{P}$ and $\hat{\vec{u}}$ are used to distinguish them from their average values, $P(\vec{r};t)$ (tagged-particle probability density), and $\vec{u}(\vec{r};t)\equiv\vec{v}(\vec{r};t)-\vec{v}(\vec{r})$ (deviation of the velocity field from shear flow). It is somewhat more convenient to work with the Fourier transforms of $\hat{P}(\vec{r})$ and $\hat{\vec{u}}(\vec{r})$. Consequently, the slow variables are chosen to be

$$y_\alpha(\vec{k})\leftrightarrow(\widetilde{\hat{P}}(\vec{k}),\widetilde{\hat{u}}_i(\vec{k})) \tag{4.2}$$

with $\widetilde{\hat{P}}$ and $\widetilde{\hat{u}}_i$ being the transforms of $\hat{P}$ and $\hat{u}_i$. The long-time behavior of the velocity autocorrelation function, Eq. (2.33), is obtained by projecting the velocity onto the set $y_\alpha(\vec{k})$ and their products. The velocity is orthogonal to $y_\alpha(\vec{k})$, and the dominant product (for small shear rate) that couples to the velocity is $\widetilde{\hat{P}}(-\vec{k})\widetilde{\hat{u}}_i(\vec{k})$. Therefore the velocity autocorrelation function is determined from the replacement

$$G_{ij}(t,\tau)\equiv\langle V_i(t-\tau)V_j(0);\tau\rangle\rightarrow\int\frac{d\vec{k}}{(2\pi)^3}\Lambda_{il}(\tau-t)\langle U_l'[\widetilde{\hat{P}}(k)\widetilde{\hat{u}}_m(-\vec{k})];\tau\rangle$$
$$\times g_{mn}^{-1}(\vec{k},\tau)\langle[\widetilde{\hat{P}}(-\vec{k};t-\tau)\widetilde{\hat{u}}_n(\vec{k};t-\tau)]U_j';\tau\rangle\ , \tag{4.3}$$

where the definition of $\vec{V}$, Eq. (2.31), has been used, and $g_{ij}(\vec{k};\tau)$ is the normalization matrix

$$g_{ij}(\vec{k};\tau)\equiv\frac{1}{\Omega}\langle[\widetilde{\hat{P}}(\vec{k})\widetilde{\hat{u}}_i(-\vec{k})][\widetilde{\hat{P}}(-\vec{k})\widetilde{\hat{u}}_j(\vec{k})];\tau\rangle$$
$$=\frac{1}{\Omega}\langle\widetilde{\hat{u}}_i(-\vec{k})\widetilde{\hat{u}}_j(\vec{k});\tau\rangle\ . \tag{4.4}$$

To simplify further, the case of asymptotically small shear rate is considered. Then the equal-time correlation functions, such as g_{ij}, may be calculated in a local equilibrium ensemble with an error of first order in the shear rate. In this limit Eq. (4.3) reduces to

$$G_{ij}(t,\tau)=\int\frac{d\vec{k}}{(2\pi)^3}\Lambda_{il}(\tau-t)$$
$$\times\langle\widetilde{\hat{P}}(-\vec{k};t-\tau)\widetilde{\hat{u}}_l(\vec{k};t-\tau)U_j'\rangle_L\ . \tag{4.5}$$

The brackets $\langle\ \rangle_L$ denote a local equilibrium average appropriate for uniform shear flow (the viscous heating is of order a^2 and is also neglected in this limit for self-consistency). The crucial assumption, implicit in selecting this particular contribution to the velocity autocorrelation function, is that the long-time dependence of (4.5) can be determined from the *macroscopic* hydrodynamic equations for $\widetilde{P}(\vec{k};t)$ and $\widetilde{\vec{u}}(\vec{k};t)$. For the nonequilibrum case considered here, $\widetilde{\hat{u}}_i(\vec{k};t)$ is the fluctuation around uniform shear flow, rather than strict equilibrium. The appropriate hydrodynamic equations are given in Appendix B. It is shown there that $G_{ij}(t,\tau)$ can be determined from the Fourier transform of the hydrodynamic equations in their Lagrangian coordinates, rather than the corresponding transformed laboratory coordinates as formulated above. This allows a close parallel to be drawn between the mode-coupling results at zero shear rate and those at finite shear rate. The results are (see Appendix B for details)

$$G_{ij}(t,\tau)=\int'\frac{d\vec{k}}{(2\pi)^3}G_{ij}(\vec{k};t-\tau)\ . \tag{4.6}$$

The prime on the integral indicates a restriction to sufficiently small values of k for hydrodynamics to be applicable, and $G_{ij}(\vec{k};t)$ is the solution to

$$\left[\frac{\partial}{\partial t}+(\nu+D)k^2(t)\right]G_{ij}(\vec{k};t)+\Delta_{il}(t)G_{lj}(\vec{k};t)=0\ ,$$
$$k_i(t)\equiv k_j\Lambda_{ji}(t)\ , \tag{4.7}$$
$$\Delta_{ij}(t)\equiv-\frac{2\Lambda_{im}(-t)k_m(t)k_l(t)}{k^2(t)}a_{lj}\ .$$

This equation for $G_{ij}(\vec{k};t)$ may be compared with that for zero shear rate,

$$\left[\frac{\partial}{\partial t}+(\nu+D)k^2\right]G_{ij}^{(0)}(\vec{k};t)=0\ . \tag{4.8}$$

The effects of finite shear rate are seen to be essentially twofold. First, the wave vector k_i is replaced by $k_i(t)=k_i-k_ja_{ji}t$. The second is a "shift" of the hydrodynamic mode

$$(\nu+D)k^2\delta_{ij}\rightarrow[(\nu+D)k^2(t)\delta_{ij}+\Delta_{ij}(t)] . \tag{4.9}$$

The significant point about this shift is that it is independent of k but first order in the shear rate a. This effect of the shear flow on mode coupling was noted in a qualitative fashion in Ref. 9, and Eq. (4.9) provides the detailed correspondence. Each of the two effects of the shear rate is due to the presence of a nonuniform Oseen-like convective term in the hydrodynamic equations.

The initial condition for Eq. (4.8) is given by

$$G_{ij}(\vec{\mathrm{k}};0)=\left\langle \widetilde{\hat{P}}(-\vec{\mathrm{k}}) \left[\widetilde{\hat{u}}_i(\vec{\mathrm{k}})-\frac{k_ik_l\widetilde{\hat{u}}_l(\vec{\mathrm{k}})}{k^2}\right] U_j' \right\rangle_L$$

$$=\frac{k_BT}{\rho}\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right] . \tag{4.10}$$

The transverse part of the velocity field has been used in Eq. (4.10) since the macroscopic dynamics was taken to be that of an incompressible fluid, i.e., $k_i\widetilde{\hat{u}}_i=0$. The solution to Eq. (4.7) is found to be

$$\begin{aligned} G_{ij}(\vec{\mathrm{k}};t)&=\frac{k_BT}{\rho}T_{il}(t)\left[\delta_{jl}-\frac{k_jk_l}{k^2}\right] ,\\ T_{ij}(t)&=e^{-b(t)}\{\delta_{ij}+2k_la_{lj}k^2[k_iI_1(t)+k_n(a_{in}-a_{ni})I_2(t)-k_na_{nm}a_{im}I_3(t)]\} \end{aligned} \tag{4.11}$$

with

$$\begin{aligned} b(t)&=(\nu+D)(k^2-k_ik_ja_{ij}t+\tfrac{1}{3}k_ik_ja_{im}a_{jm}t^2) ,\\ I_1(t)&=\frac{-2k_ia_{ij}}{E}\left[\frac{k_j(t)}{k^2(t)}-\frac{k_j}{k^2}\right]+\frac{4k_ik_ja_{im}a_{jm}}{E^{3/2}}\left[\tan^{-1}\left[\frac{2k_ik_ja_{ij}}{\sqrt{E}}\right]-\tan^{-1}\left[\frac{2k_i(t)k_j(t)a_{ij}}{\sqrt{E}}\right]\right] ,\\ I_2(t)&=\frac{-2k_i}{E}\left[\frac{k_i(t)}{k^2(t)}-\frac{k_i}{k^2}\right]+\frac{4k_ik_ja_{ij}}{E^{3/2}}\left[\tan^{-1}\left[\frac{2k_ik_ja_{ij}}{\sqrt{E}}\right]-\tan^{-1}\left[\frac{2k_i(t)k_j(t)a_{ij}}{\sqrt{E}}\right]\right] ,\\ I_3(t)&=(k_lk_ma_{ln}a_{mn}E)^{-1}\left[\frac{2k^2k_i(t)k_j(t)a_{ij}+Et}{k^2(t)}-\frac{2k^2k_ik_ja_{ij}}{k^2}\right]\\ &\quad+\frac{4k^2}{E^{3/2}}\left[\tan^{-1}\left[\frac{2k_ik_ja_{ij}}{\sqrt{E}}\right]-\tan^{-1}\left[\frac{2k_i(t)k_j(t)a_{ij}}{\sqrt{E}}\right]\right] ,\\ E&=4k_lk_ma_{li}a_{mj}(k^2\delta_{ij}-k_ik_j) . \end{aligned} \tag{4.12}$$

To calculate the mode-coupling contribution to $D_{ij}^*(a,w)$, Eq. (2.35) is first rewritten as

$$\widetilde{D}_{ij}^*(a;w)=\delta_{ij}+\int_0^\infty dt\{\cos(wt)[\underline{\Delta}(t)\underline{G}(t)\underline{\Delta}^T(-t)]_{ij}-G_{ij}^{(0)}(t)\}D^{-1} \tag{4.13}$$

with $G_{ij}^{(0)}(t)$ equal to $G_{ij}(t)$ at zero shear rate, and for large t

$$G_{ij}(t)=\int{}' \frac{d\vec{\mathrm{k}}}{(2\pi)^3}G_{ij}(k,t)\rightarrow\int{}' \frac{d\vec{\mathrm{k}}}{(2\pi)^3}\frac{k_BT}{\rho}T_{il}(t)\left[\delta_{li}-\frac{k_lk_j}{k^2}\right] . \tag{4.14}$$

The simplest component of the diffusion tensor is that for i and j along the direction of the velocity gradient

$$D^*(a;w)\equiv a_{il}a_{im}\widetilde{D}_{lm}^*(a;w)/a^2 . \tag{4.15}$$

To be more explicit a representation of the shear rate tensor is chosen,

$$a_{ij}=a\delta_{ix}\delta_{jy} , \tag{4.16}$$

so that the x axis is chosen along the direction of flow and the y axis is along the direction of the gradient. Use of (4.14) in (4.15) then gives

$$D^*(a;w)\rightarrow1+\int_0^\infty dt\int{}' \frac{d\vec{\mathrm{k}}}{(2\pi)^3}[T_{yl}(t)\cos(wt)-T_{yl}^{(0)}(t)]\frac{k_BT}{\rho D}\left[\delta_{ly}-\frac{k_lk_y}{k^2}\right] , \tag{4.17}$$

where $T_{ij}^{(0)}$ is the zero-shear-rate limit of $T_{ij}(t)$. The specific form of this tensor, given by Eqs. (4.11) and (4.12), simplifies considerably for the components in Eq. (4.17), leading to

$$D^*(a;w)\rightarrow 1+\int_0^\infty dt\int\frac{d\vec{k}}{(2\pi)^3}\Theta(k_0-k)\left[\frac{k^2-k_y^2}{k^2}\right]\frac{k_BT}{\rho D}\left[e^{-b(t)}\frac{k^2}{k^2(t)}\cos(wt)-e^{-(\nu+D)k^2t}\right], \tag{4.18}$$

where now the restriction to small-k values has been made explicit through introduction of the step function $\Theta(k_0-k)$. The characteristic cutoff k_0 is typically of the order of the inverse mean-free path. A change of variables, $\vec{k}\rightarrow\vec{k}(-t)$ for the integral of the first term in the brackets, and a scaling of the magnitude of k gives

$$D^*(a;w)\rightarrow 1+\frac{k_BT}{\rho D[4\pi(\nu+D)]^{3/2}} \times\int_0^\infty dt\,t^{-3/2}\int\frac{d\Omega}{4\pi}(1-e_y^2)\frac{4}{\sqrt{\pi}}\int_0^\infty dk\,k^2e^{-k^2}\left[\frac{\Theta(k_1(t)-k)}{\alpha^{3/2}(at)}\cos(wt)-\Theta(k_0(t)-k)\right]. \tag{4.19}$$

The effective cutoffs $k_1(t)$ and $k_0(t)$ are defined by

$$k_1(t)=k_0(t)\left[\frac{1+e_ye_xat+\frac{1}{3}(e_xat)^2}{1+e_ye_xat+(e_xat)^2}\right]^{1/2},$$
$$k_0^2(t)=(\nu+D)k^2t, \tag{4.20}$$

and

$$\alpha(at)\equiv 1+e_ye_xat+\tfrac{1}{3}(e_xat)^2. \tag{4.21}$$

Also, e_x,e_y,e_z are components of the unit vector $\vec{k}/|\vec{k}|$, and $d\Omega$ denotes the associated solid angle integration. It is seen from (4.20) that the shear-rate-dependent cutoff $k_1(t)$ is always of the order of $k_0(t)$ for all shear rates. Furthermore, the effective range of the k integral of (4.19) is $k<1$. Therefore, for large t, $k_0(t)>1$ and the above is independent of all cutoffs. The k integral can be performed in this limit to give, finally,

$$D^*(w,a)\rightarrow 1+\frac{k_BT}{\rho D[4\pi(\nu+D)]^{3/2}} \times\int_0^\infty dt\,t^{-3/2}\int\frac{d\Omega}{4\pi}(1-e_y^2) \times[\alpha^{-3/2}(at)\cos(wt)-1]. \tag{4.22}$$

The large-time behavior ("tails") of the velocity autocorrelation function due to mode coupling is reflected by the factor of $t^{-3/2}$ in Eq. (4.22). This slow decay is controlled by two other functions in the integrand, one depending on (at) and the other on (wt). The long-time tails will therefore imply a nonanalytic dependence on either shear rate a or frequency w, depending on whether $a\gg w$ or $w\gg a$, respectively. To make this more evident, Eq. (4.22) can be written in terms of a universal crossover function between these two limits:

$$D^*(w,a)\rightarrow 1-C(w/w_0)^{1/2}\Delta(a/w), \tag{4.23}$$

where the dimensionless constant C and frequency w_0 are defined by

$$C\equiv\frac{2\sqrt{2\pi}}{3n}\left[\frac{w_0}{4\pi(\nu+D)}\right]^{3/2},$$
$$w_0\equiv\frac{k_BT}{mD}, \tag{4.24}$$

and the crossover function $\Delta(x)$ is

$$\Delta(x)\equiv(2\pi)^{-1/2}\int_0^\infty dt\,t^{-3/2}[1-\gamma(xt)\cos t],$$
$$\gamma(t)\equiv\frac{3}{4\pi}\int_0^\infty d\phi\int_0^1 dy(\cos^2\phi+y^2\sin^2\phi)[1+(1-y^2)t(\sin\phi\cos\phi+\tfrac{1}{3}t\cos^2\phi)]^{-3/2}. \tag{4.25}$$

It is readily verified that $\Delta(0)=1$ and $\Delta(x)\sim\sqrt{x}$ for large x. This leads to the limiting behavior for $D^*(a;w)$,

$$D^*(a;w)\rightarrow\begin{cases}1-C(w/w_0)^{1/2}, & a/w\ll 1\\ 1-C'(a/w_0)^{1/2}, & a/w\gg 1.\end{cases} \tag{4.26}$$

This result for $a/w\ll 1$ is the usual prediction for the nonanalytic frequency dependence of the self-diffusion coefficient in an equilibrium fluid. The second result, for $a/w\gg 1$, is analogous to that obtained for the nonanalytic dependence of the nonlinear shear viscosity on shear rate. The constant C' characterizing this limit is given by

$$C'\equiv C(2\pi)^{-1/2}\int_0^\infty dt\,t^{-1/2}[1-\gamma(t)]$$
$$\sim 0.46C. \tag{4.27}$$

Therefore, as in the case of shear viscosity, the nonanalytic dependence of $D^*(a;w)$ on frequency at zero shear rate is the same as its dependence on shear rate at zero frequency. The coefficients characterizing these square-root forms are different, however. The specific relationship of C' to C is given by the first line of Eq. (4.27) and, in contrast to the Goddard-Miller model described in the next section, depends in detail on the hydrodynamics of shear flow.

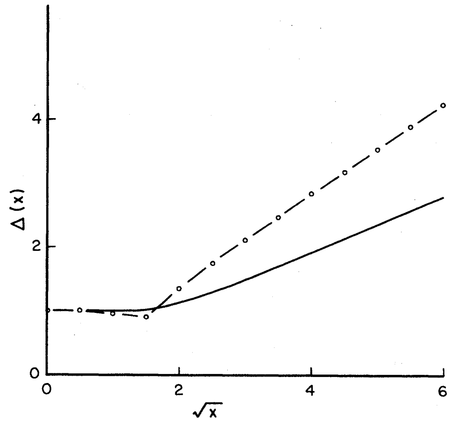

FIG. 2. Function $\Delta(x)$, given by Eq. (4.25) (——), and as given by the Goddard-Miller model (—○—).

When *both* frequency and shear rate are finite, the function $\Delta(x)$ in Eq. (4.23) describes the transition region between the above two limits. This function is universal in the sense that it is independent of all physical parameters. Its form is determined only by the particular nonequilibrium state of uniform shear flow. Consequently, all fluids whose macroscopic dynamics is governed by the Navier-Stokes equations will lead to asymptotic diffusion characterized by the same function, $\Delta(x)$. Figure 2 illustrates the smooth transition between frequency-dominated and shear-rate-dominated limits.

V. GODDARD-MILLER MODEL

To model the viscoelastic and non-Newtonian properties of complex rheological fluids, a relatively simple relationship between the irreversible part of the stress tensor, t_{ij}, and the strain tensor γ_{ij} has been used,[30,31]

$$t_{ij}(t) = -\int_0^t d\tau[2C(t-\tau)\Gamma_{ij}(t,\tau)] , \tag{5.1}$$

where $\Gamma_{ij}(t,\tau)$ is the strain rate tensor in the corotating frame,

$$\begin{aligned}\Gamma_{ij}(t,\tau) &= [\underline{R}(t-\tau)\underline{\gamma}\,\underline{R}^{-1}(t-\tau)]_{ij} ,\\ \gamma_{ij} &= \frac{1}{2}\left[\frac{\partial U_i}{\partial r_j}+\frac{\partial U_j}{\partial r_i}\right] .\end{aligned} \tag{5.2}$$

Here $R_{ij}(t)$ is the rotation tensor for transformation to a frame rotating at an angular velocity equal to that of the fluid (one-half the fluid vorticity). The response function $C(t)$ is taken to be the same as that for a fluid with no vorticity, i.e., it is the response function for *linear* viscoelasticity. Consider a flow with time-independent vorticity,

$$\begin{aligned}\frac{\partial}{\partial r_j}U_i &= \gamma_{ij}(t)+w_{ij} ,\\ w_{ij} &= \tfrac{1}{2}(a_{ij}+a_{ji}) ,\end{aligned} \tag{5.3}$$

where a_{ij} is taken to be the shear rate tensor of Eq. (4.16). The rotation matrices are easily evaluated for this case and Eq. (5.1) simplifies to

$$t_{xy}(t) = -\int_0^t d\tau\{2C(t-\tau)\cos[a(t-\tau)]\gamma_{xy}(\tau)\} . \tag{5.4}$$

The corresponding frequency and shear-rate-dependent viscosity is then defined by

$$\eta(w,a) = \int_0^\infty dt\,\cos(wt)C(t)\cos(at) . \tag{5.5}$$

This model can be applied in an analogous way to diffusion in the flow field (5.3). The irreversible probability current J^* is assumed to be related to the gradient of the probability density in the corotating frame,

$$J_i^* = -\int_0^t dt\,G_0(t-\tau)R_{ij}(t-\tau)\frac{\partial}{\partial r_j}P(\tau) , \tag{5.6}$$

where $G_0(t-\tau)$ is the *equilibrium* velocity autocorrelation function. The associated frequency and shear-rate-dependent diffusion coefficient is then

$$D_{ij}(a;w) = \int_0^\infty dt\,\cos(wt)G_0(t)R_{ij}(t) . \tag{5.7}$$

In particular, the component along the direction of the velocity gradient is

$$D_{yy}(a;w) = \int_0^\infty dt\,\cos(wt)G_0(t)\cos(at/2) . \tag{5.8}$$

The small w and a behavior is governed by the long-time behavior of $G_0(t)$. Use of the equilibrium mode-coupling form for $G_0(t)$ in (5.8) then leads to the result (4.23), except $\gamma(t)$ is replaced by

$$\gamma(t)\to\cos(at/2) . \tag{5.9}$$

Similarly, the asymptotic behavior of this Goddard-Miller model is the same as Eq. (4.26), except that $C'=C/\sqrt{2}\sim 0.71C$ [note that this result differs by a factor of $1/\sqrt{2}$ from that of Ref. 22; the origin of this difference is the factor of $\frac{1}{2}$ in the argument of the cosine in Eq. (5.9) that was omitted in Ref. 22]. For finite frequencies and shear rate, the Goddard-Miller form for the function $\Delta(x)$ is also shown in Fig. 2.

VI. DISCUSSION

A formal definition of the nonlinear diffusion coefficient for shear flow has been identified in a form suitable for theoretical analysis (e.g., molecular rather than Taylor diffusion) and for nonequilibrium computer simulation. Typically, in a nonequilibrium simulation the appropriate current (here $\vec{J}^*$) is divided by the corresponding "force" (here $\vec{\nabla}P$) to determine the nonlinear transport coefficient. For small gradients this procedure should agree with the Green-Kubo expressions for transport coefficients as *equilibrium* time correlation functions. The results of Sec. II suggest a means for unifying the study of linear and nonlinear transport by identifying the appropriate generalization of the Green-Kubo expressions to the general nonequilibrium state for shear flow. Specifically, Eqs. (2.26) and (2.27) define a computer simulation problem for the determination of the diffusion tensor as a fluctuation expression in the *nonequilibrium* state, analogous to current equilibrium simulations for linear transport coefficients. The analysis given here for self-diffusion can be extended to other transport properties for shear flow as well (e.g., nonlinear thermal conductivity and viscosity).

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APPENDIX A: TRANSLATIONAL INVARIANCE

The objective here is to prove that the probability density in the Lagrangian frame, $P'(q,t)$, is translationally invariant. A related result has been obtained by Onuki and Kawasaki.[32] Equation (2.18) may be written more explicitly

$$
\begin{aligned}
P'(\vec{q};t) &\equiv P'(\vec{q}-\vec{r}_0,\vec{r}_0;t)\\
&= \int d\vec{Q}\,d\vec{U}\,d\Gamma\;\Omega\rho(\vec{U}-\vec{v}(\vec{Q}),\Gamma;0)\\
&\qquad\times\delta(\vec{Q}-\vec{r}_0)\delta(\vec{Q}(t)-\vec{Q}-(\vec{q}-\vec{r}_0))\;, \qquad \text{(A1)}
\end{aligned}
$$

where $\vec{Q}\equiv\vec{Q}(0)=\vec{R}$ and $\Gamma\equiv\{\vec{r}_\alpha,\vec{p}_\alpha\}$ denotes a phase point for the positions and momenta of the fluid particles. A change of variables,

$$
\vec{U}\,'=\vec{U}-\vec{v}(\vec{Q}),\quad \vec{p}\,'_\alpha=\vec{p}_\alpha-m\vec{v}(q_\alpha)\;, \qquad \text{(A2)}
$$

then leads to

$$
\begin{aligned}
&P'(\vec{q}-\vec{r}_0,\vec{r}_0;t)\\
&\quad= \int d\vec{Q}\,d\vec{U}\,'d\Gamma'\;\Omega\rho(\vec{U}\,',\Gamma;0)\\
&\qquad\times\delta(\vec{Q}-\vec{r}_0)\delta(\vec{Q}(t)-\vec{Q}-(\vec{q}-\vec{r}_0))\;, \qquad \text{(A3)}
\end{aligned}
$$

where $d\Gamma'\equiv\{\vec{r}_\alpha,\vec{p}\,'_\alpha\}$ and it is understood that $\vec{Q}(t)$ is now a function of $\vec{Q}$, $\vec{U}\,'$, Γ', and t. The equations of motion in these variables are readily obtained from the definition (2.17):

$$
\begin{aligned}
&\frac{d}{dt}Q_i(t)=\Lambda_{ij}(t)U'_j(t)\;,\\
&\frac{d}{dt}U'_i+a_{ij}U'_j(t) \qquad\qquad \text{(A4)}\\
&\qquad=\Lambda_{ij}(t)\sum_\alpha F_{\alpha j}[\underline{\Delta}^{-1}(t)(Q(t)-q_\alpha(t))]\;,
\end{aligned}
$$

where $\vec{F}_i(\vec{r})$ is the interatomic force between a pair of particles, and $\vec{q}(t)$ is defined in a manner similar to $\vec{Q}(t)$,

$$
\vec{q}_\alpha(t)=\vec{r}_\alpha(t)-\vec{v}(\vec{r}_\alpha(t))\;. \qquad \text{(A5)}
$$

The equations for $\vec{q}_\alpha(t)$ and $\vec{p}\,'_\alpha(t)$ are formally the same as (A4). Consequently, from the translational invariance of (A4), $\vec{Q}(t)$ transforms under the translation $\vec{Q}\to\vec{Q}+\vec{x}$ as $\vec{Q}(t)\to\vec{Q}(t)+\vec{x}$. [Note that this property does not hold for the laboratory coordinate $\vec{R}(t)$, as a function of $\vec{U}\,'(t)$, since it obeys the equation

$$
\frac{d}{dt}\vec{R}(t)=\Lambda_{ij}(t)U'_j(t)+a_{ij}R_j(t) \qquad \text{(A6)}
$$

which is *not* translationally invariant. The choice of $\vec{U}\,'$ rather than $\vec{U}$ is required for invariance of the ensemble $\rho(\vec{U}\,',\Gamma;0)$.] A change of variables, $\vec{Q}=\vec{Q}-\vec{x}$ in (A3), then gives the desired result

$$
P'(\vec{q}-\vec{r}_0,\vec{r}_0;t)=P'(\vec{q}-\vec{r}_0,\vec{r}_0+\vec{x};t) \qquad \text{(A7)}
$$

and $P'(\vec{q}-\vec{r}_0,\vec{r}_0;t)$ depends on $\vec{r}_0$ only through $\vec{q}-\vec{r}_0$. Also, it is simply related to an average over the uniform ensemble, (2.4), by the identity

$$
\begin{aligned}
P'(\vec{q}-\vec{r}_0,\vec{r}_0;t)&=\Omega^{-1}\int d\vec{x}\,P'(\vec{q}-\vec{r}_0,\vec{r}_0+\vec{x};t)\\
&=\int d\vec{Q}\,d\vec{U}\,d\Gamma\,\rho(\vec{U}\,',\Gamma;0)\\
&\qquad\times\delta(\vec{Q}(t)-\vec{Q}-(\vec{q}-\vec{r}_0)) \qquad \text{(A8)}
\end{aligned}
$$

or

$$
P'(\vec{q};t)=\langle\delta(\vec{Q}(t)-\vec{Q}-(\vec{q}-\vec{r}_0));0\rangle\;, \qquad \text{(A9)}
$$

which is Eq. (2.19) used in the text.

APPENDIX B: SOLUTIONS TO HYDRODYNAMIC EQUATIONS

The hydrodynamic equations for the probability density $P(\vec{r};t)$ and the velocity field $\vec{v}(\vec{r};t)$ for an incompressible fluid are

$$
\begin{aligned}
&\left[\frac{\partial}{\partial t}+\vec{v}(\vec{r};t)\cdot\vec{\nabla}\right]P(\vec{r};t)-D_{ij}\frac{\partial^2}{\partial r_i\,\partial r_j}P(\vec{r};t)=0\;,\\
&\left[\frac{\partial}{\partial t}+\vec{v}(\vec{r};t)\cdot\vec{\nabla}\right]\vec{v}_i(\vec{r};t)+\frac{1}{\rho}\frac{\partial}{\partial r_i}p(\vec{r};t)-\nu\nabla^2 v_i=0\;, \qquad \text{(B1)}\\
&\vec{\nabla}\cdot\vec{v}(\vec{r};t)=0\;,
\end{aligned}
$$

where $\nu\equiv\eta/\rho$ is the kinematic viscosity, ρ is the density, and $p(\vec{r};t)$ is the pressure. To calculate the mode-coupling contributions in Sec. IV these equations may be linearized about uniform shear flow:

$$
\begin{aligned}
&\left[\frac{\partial}{\partial t}+a_{ij}r_j\frac{\partial}{\partial r_i}\right]P(\vec{r};t)-D_{ij}\frac{\partial^2}{\partial r_i\,\partial r_j}P(\vec{r};t)=0\;,\\
&\left[\frac{\partial}{\partial t}+a_{lj}r_j\frac{\partial}{\partial r_l}-\eta\nabla^2\right]u_i(\vec{r};t)+a_{ij}u_j(\vec{r};t)\\
&\qquad\qquad+\frac{1}{\rho}\frac{\partial}{\partial r_i}p(\vec{r};t)=0\;, \qquad \text{(B2)}\\
&\vec{\nabla}\cdot\vec{u}(\vec{r};t)=0\;.
\end{aligned}
$$

Here $u(\vec{r};t)$ is the deviation of the velocity from that for uniform shear flow,

$$u_i(\vec{r};t)=v_i(\vec{r};t)-a_{ij}r_j \; . \tag{B3}$$

An equation for the pressure follows from the divergence of the equation for $u_i(\vec{r};t)$:

$$\nabla^2 p(\vec{r};t)+2\rho a_{ij}\frac{\partial}{\partial r_i}u_j=0 \; . \tag{B4}$$

The set of equations (B2) and (B4) are most easily solved by making a transformation to the Lagrangian coordinates (2.12) to give

$$\begin{gathered}
\left[\frac{\partial}{\partial t}-D_{ij}\Lambda_{ki}(t)\Lambda_{lj}(t)\frac{\partial^2}{\partial q_k\partial q_l}\right]P'(\vec{q};t)=0 \; , \\
\left[\frac{\partial}{\partial t}-\nu\Lambda_{kj}(t)\Lambda_{lj}(t)\frac{\partial^2}{\Phi q_k\partial q_l}\right]u_i'(\vec{q};t)+a_{ij}u_j'(\vec{q};t) \\
+\frac{1}{\rho}\Lambda_{ji}(t)\frac{\partial}{\partial q_j}p'(\vec{q};t)=0 \; , \\
\Lambda_{ji}(t)\frac{\partial}{\partial q_j}u'(\vec{q};t)=0 \; , \\
\Lambda_{ki}(t)\Lambda_{li}(t)\frac{\partial^2}{\partial q_k\partial q_l}p'(\vec{q};t)+2\rho a_{ij}\Lambda_{ki}(t)\frac{\partial}{\partial q_k}u_j'=0 \; .
\end{gathered} \tag{B5}$$

The prime on a function denotes the same function with the prime expressed in the new coordinates, e.g.,

$$P'(\vec{q};t)\equiv P(\vec{r};t) \; , \tag{B6}$$

etc. Define the Fourier transform of a function of $\vec{q}$ by

$$\tilde{f}(\vec{k})\equiv\int d\vec{q}\, e^{i\vec{k}\cdot\vec{q}}f(\vec{q}) \; . \tag{B7}$$

The Fourier transform of Eqs. (B5) then gives

$$\begin{gathered}
\left[\frac{\partial}{\partial t}+D_{ij}k_i(t)k_j(t)\right]\tilde{P}'(\vec{k};t)=0 \; , \\
\left[\frac{\partial}{\partial t}+\nu k^2(t)\right]\tilde{u}_i'(\vec{k};t)+a_{ij}\tilde{u}_j'(\vec{k};t)-\frac{1}{\rho}ik_i(t)\tilde{p}'(\vec{k};t)=0 \; , \\
i\vec{k}(t)\cdot\vec{\tilde{u}}'(\vec{k};t)=0 \; , \\
k^2(t)\tilde{p}'(\vec{k};t)+2\rho a_{ij}ik_i(t)\tilde{u}_j'(\vec{k};t)=0 \; .
\end{gathered} \tag{B8}$$

Here $\vec{k}(t)$ is defined by

$$k_i(t)=k_j\Lambda_{ji}(t) \; . \tag{B9}$$

The pressure can be eliminated from the velocity equation to give

$$\left[\frac{\partial}{\partial t}+\nu k^2(t)\right]\tilde{u}_i'(\vec{k};t)+a_{ij}\tilde{u}_j'(\vec{k};t) -2\frac{k_i(t)k_l(t)}{k^2(t)}a_{lj}\tilde{u}_j'(\vec{k};t)=0 \; . \tag{B10}$$

To set these results in a form most closely related to those for zero shear rate a final transformation on the velocity can be made, as suggested by Eq. (2.32):

$$u_i''(\vec{k};t)=\Lambda_{ij}(-t)\tilde{u}_j'(\vec{k};t) \; . \tag{B11}$$

Also, to lowest order in the shear rate, D_{ij} may be replaced by its equilibrium value $D\delta_{ij}$. The hydrodynamic equations for shear flow then become

$$\begin{gathered}
\left[\frac{\partial}{\partial t}+Dk^2(t)\right]\tilde{P}'(\vec{k};t)=0 \; , \\
\left[\frac{\partial}{\partial t}+\nu k^2(t)\right]\tilde{u}_i''(\vec{k}';t)+\Delta_{ij}(t)\tilde{u}_j''(\vec{k}';t)=0 \; ,
\end{gathered} \tag{B12}$$

with

$$\Delta_{ij}(t)\equiv-2\Lambda_{im}(-t)\frac{k_m(t)k_l(t)}{k^2(t)}a_{lj} \; . \tag{B13}$$

For $a=0$, Δ_{ij} vanishes, $\vec{k}(t)\to\vec{k}$, and the linearized hydrodynamic equations for fluctuations around equilibrium are regained.

The solutions to equations (B13) are obtained by integration,

$$\begin{gathered}
\tilde{P}'(\vec{k};t)=P'(\vec{k};0)\exp\left[-\int_0^t d\tau\, Dk^2(\tau)\right] \; , \\
\tilde{u}_i'(\vec{k};t)=\Lambda_{il}(t) \\
\times\left[\exp\left[-\int_0^t d\tau[\nu k^2(\tau)+\Delta(\tau)]\right]\right]_{lj}\tilde{u}_j'(\vec{k};0) \; .
\end{gathered} \tag{B14}$$

It is not necessary to transform this result back to the laboratory coordinates for the purposes here because of the identity

$$\int d\vec{k}\,\tilde{P}(-\vec{k};t)\tilde{u}_i(\vec{k};t)=\int d\vec{k}\,\tilde{P}'(-\vec{k};t)\tilde{u}_i'(\vec{k};t) \; , \tag{B15}$$

as follows from the definition of the transformation to Lagrangian coordinates and the fact that the Jacobian is unity. Therefore, the mode-coupling integral of interest is [Eq. (4.6)]

$$\int\frac{d\tilde{k}}{(2\pi)^3}\Lambda_{il}(-t)\langle\tilde{\hat{P}}(-\vec{k};t)\tilde{\hat{u}}_l(\vec{k};t)U_j'\rangle_L \equiv\int\frac{d\vec{k}}{(2\pi)^3}G_{ij}(\vec{k};t) \; , \tag{B16}$$

where $G_{ij}(\vec{k};t)$ is the solution to

$$\left[\frac{\partial}{\partial t}+(\nu+D)k^2(t)\right]G_{ij}(\vec{k};t)+\Delta_{il}(t)G_{lj}(\vec{k};t)=0 \tag{B17}$$

with initial condition

$$\begin{aligned}
G_{ij}(\vec{k};0)&=\langle P(-\vec{k};0)\tilde{\hat{u}}_i(\vec{k};0)U_j\rangle_L \\
&\to\left\langle P(-k)\left[\tilde{\hat{u}}_i(k)-k_i\frac{\vec{k}\cdot\tilde{\hat{u}}(\vec{k})}{k^2}\right]U_j\right\rangle_L \\
&=\frac{k_BT}{\rho}\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right] \; .
\end{aligned} \tag{B18}$$

The second line follows from the condition $\vec{k}\cdot\tilde{\hat{u}}(\vec{k})=0$, for an incompressible fluid. The solution to (B17) is now straightforward, but lengthy, to obtain and only the result is quoted in Sec. IV.

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