PHYSICAL REVIEW A VOLUME 39, NUMBER 3 FEBRUARY 1, 1989

Fluctuations and dissipation in a fluid under shear: Linear dynamics

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(Received 23 June 1988)

A set of nonlinear Langevin equations for fluctuations of the local conserved densities in a fluid under shear is proposed. These equations are a model for the extension of hydrodynamics to very short wavelengths at liquid densities. The hydrodynamic modes associated with the linearized equations are studied as a function of wave vector and shear rate. The degeneracy of the viscous shear modes is lifted by the shear, and one of these modes combines with the heat mode to form a propagating pair. As an example of nonequilibrium fluctuations, the dynamic structure factor is calculated for several values of frequency and wave vector. At large shear rates one pair of propagating modes becomes unstable at a wavelength of the order of the particle size. This instability is suggested as a possible explanation for a shear-induced disorder-order transition seen in computer simulations. Nonlinear mode-coupling effects are studied elsewhere.

I. INTRODUCTION

Long-wavelength, low-frequency fluctuations in an equilibrium fluid are well described by the linear Navier-Stokes hydrodynamics equations. This macroscopic description of dynamical fluctuations is essentially Onsager's regression hypothesis.[1] Its theoretical basis and experimental verification have been established for a wide class of systems. At higher frequencies and shorter wavelengths, as probed by neutron scattering, for example, it might be expected that a hydrodynamic description would fail. However, hydrodynamics is relevant for wavelengths long compared to the mean free path, and at liquid densities the latter is comparable to or smaller than the atomic size. In this case, hydrodynamics is applicable to phenomena typically thought of as microscopic. Of course, the Navier-Stokes form must be modified to account for atomic structure at short wavelengths, but a closed set of equations for the local conserved densities still can be obtained.[2] Recently, the validity of this hydrodynamic approach for the calculation of the equilibrium dynamic structure factor has been shown.[3] Also, its applicability at atomic dimensions has been demonstrated by comparison with computer simulation results for a hard-sphere fluid.[4]

The objective here is to extend this "molecular hydrodynamics" in two directions. First, the linear deterministic equations are extended to nonlinear Langevin equations. Fluctuation renormalization of the nonlinearities is well known to be important at long wavelengths[5] and this effect should be included in the generalized hydrodynamics as well. The second extension is to include fluctuations about nonequilibrium stationary states. This is difficult to explore in general since the properties for such states can be quite different in each case. To be more specific, we specialize to a fluid in uniform shear flow. This choice is motivated by nonequilibrium computer simulation methods developed for this stationary state.[6] Although idealized, it provides a rare example of a nonequilibrium state that can be characterized in detail at the microscopic level.

Most discussions of Navier-Stokes-Langevin equations, or the associated Fokker-Planck equations, are based on a phenomenological extension of known macroscopic equations to a stochastic description.[7] Here, we need to know the effects of atomic structure at short wavelengths, so a more detailed microscopic derivation is required. To make this problem tractible we consider only the exact short-time equations for a hard-sphere fluid. This approximation implies no *a priori* restrictions on either density or wavelength. The short-time limit is quite restrictive for continuous potentials, leading to a simple mean-field approximation. However, for hard spheres and other discontinuous potentials there is a finite momentum change in an infinitesimal time and a reasonable account of collisional transport is obtained. At the level of kinetic theory (single-particle phase-space densities) the short-time limit leads to a generalized Enskog equation[8] that is known to describe well even long-time properties like transport coefficients. For the local conserved densities, these short-time equations provide a basis for extending hydrodynamics to include very-short-wavelength excitations.[9] This should be contrasted with other generalizations of hydrodynamics where the thermodynamic derivatives are replaced by the corresponding wave-vector-dependent correlation functions. Here, in addition to thermodynamic generalizations, an explicit wave-vector dependence for the transport coefficients is also obtained. Furthermore, the simplicity of a mean-field approximation is maintained in the sense that only time-independent expressions need to be calculated. It is one of the few methods for describing a fluid at high densities for spatial excitations extending from the order of the correlation length to macroscopic length scales.

In Sec. II the formal Langevin equations for a general class of phase functions are obtained, indicating the special treatment required for hard spheres. The short-time limit of these equations is indicated and a fluctuation-dissipation relation with white noise is obtained in this limit. These results are then specialized to describe fluctuations in stationary states. The case of uniform shear flow is then considered, and the phase functions are chosen to be the local conserved densities (mass, energy, and momentum) and their bilinear products. The matrix elements for the linear part of the hydrodynamic equations are calculated to first order in the shear rate as a function of the density and wave vector.

In Sec. III the hydrodynamic modes associated with the linear equations are calculated. At zero shear rate these are the extensions to short wavelengths of the usual degenerate pair of diffusive shear modes, two propagating sound modes, and a diffusive heat mode. For nonzero shear rate the degeneracy is broken by a coupling of longitudinal and transverse momentum components. The two sound modes still occur, but one of the shear modes combines with the heat mode to form another propagating pair. Thus the decay of short-wavelength fluctuations around shear flow is quite unusual, in contrast to previous studies at long wavelengths.[10] This is illustrated by calculation of the static and dynamic structure factor as a function of the frequency at several wave vectors and shear rates. A distortion of the static structure is obtained for wave vectors along the direction of the velocity gradient, in contrast to simpler models.

The computer simulations of uniform shear flow allow calculations for states very far from equilibrium. Perhaps the most unexpected result of such studies is a transition of the fluid to an ordered state at large shear rates.[11] Since no such transition is evident in the equilibrium state for hard spheres, its origin is quite mysterious. In Sec. IV it is shown that there is a short-wavelength instability in the hydrodynamic equations at large shear rates.[12,13] The magnitude and direction of the unstable wave vector as well as the critical shear rate are in qualitative agreement with the computer simulation results. The approximation involved in these equations makes their application at large shear rates uncertain, but they suggest that such an instability may be the mechanism responsible for transition to the ordered state.

II. LANGEVIN EQUATIONS

Formal Langevin equations for a chosen set of variables $\{\psi_\alpha\}$ are readily obtained from the Zwanzig-Mori projection operator identities.[14] Most applications have been to describe fluctuations in equilibrium states interacting via continuous interparticle potentials. In this section we review briefly this formalism to indicate the changes required for generalization to nonequilibrium stationary states and discontinuous potentials (e.g., hard spheres). Also, the primary approximations are introduced and discussed.

The time dependence of the variables $\{\psi_\alpha\}$ is generated by the Liouville operators, L_+ or L_-,

$$\psi_\alpha(t)=e^{L_\pm t}\psi_\alpha \ , \tag{2.1}$$

where L_+ applies for $t>0$ and L_- applies for $t<0$. These two operators are the same for continuous potentials, but for discontinuous potentials they are different. Also, it is understood that $L_\pm$ may contain contributions from nonconservative external forces and boundary conditions required to generate a prescribed stationary state. The explicit forms of these operators for the case of hard spheres are given in Appendix A. The Langevin equation of interest is that for the fluctuations of $\{\psi_\alpha\}$ about their average value in the stationary state,

$$\tilde{\psi}_\alpha \equiv \psi_\alpha - \langle \psi_\alpha \rangle \ , \tag{2.2}$$

$$\langle \psi_\alpha \rangle \equiv \int d\Gamma\, \rho(\Gamma)\psi_\alpha(\Gamma) \ , \tag{2.3}$$

where ρ denotes the stationary-state probability density in phase space. A projection operator onto the subspace spanned by $\{\psi_\alpha\}$ is defined by

$$PX \equiv \langle X\tilde{\psi}^*_\beta \rangle w^{-1}_{\beta\alpha}\tilde{\psi}_\alpha \ , \tag{2.4}$$

$$w_{\alpha\beta} \equiv \langle \tilde{\psi}_\alpha \psi^*_\beta \rangle \ , \tag{2.5}$$

where $X(\Gamma)$ is an arbitrary phase function. The following operator identity is easily verified by direct differentiation:

$$e^{L_+ t}=e^{L_+ t}P+\int_0^t d\tau\, e^{L_+(t-\tau)}PL_+e^{L'\tau}Q+e^{L't}Q \ , \qquad t\geq 0 \tag{2.6}$$

Here, $Q=1-P$ and $L'=QL_+Q$. The Langevin equation for $t>0$ now follows directly from Eqs. (2.1), (2.4), and (2.6),

$$\frac{\partial}{\partial t}\tilde{\psi}_\alpha(t)+\Omega_{\alpha\beta}\tilde{\psi}_\beta(t)+\int_0^t d\tau\, \gamma_{\alpha\beta}(\tau)\tilde{\psi}_\beta(t-\tau)=f_\alpha(t) \ , \tag{2.7}$$

with the definitions

$$\begin{aligned}\Omega_{\alpha\beta}&=-\langle [L_+\tilde{\psi}_\alpha]\tilde{\psi}^*_\gamma \rangle w^{-1}_{\gamma\beta} \ ,\\ \gamma_{\alpha\beta}&=-\langle [L_+e^{L't}QL_+\tilde{\psi}_\alpha]\tilde{\psi}^*_\sigma \rangle w^{-1}_{\sigma\beta} \ ,\\ f_\alpha(t)&\equiv e^{L't}QL_+\tilde{\psi}_\alpha \ .\end{aligned} \tag{2.8}$$

The source term $f_\alpha(t)$ has the interpretation of a "stochastic force," or "noise," since it is orthogonal to the set $\{\psi_\alpha\}$ in the sense,

$$\langle f_\alpha(t)\tilde{\psi}^*_\beta \rangle=0, \quad t\geq 0 \ . \tag{2.9}$$

Also, for an appropriate choice of variables the time scale for variations in $f_\alpha(t)$ is expected to be short compared to that for $\{\psi_\alpha\}$.

The first approximation for our model is to replace the Langevin equation, (2.7), by its short-time limit. Assuming $\gamma_{\alpha\beta}(t)$ is nonsingular at $t=0^+$, the result is

$$\frac{\partial}{\partial t}\tilde{\psi}_\alpha(t)+\Omega_{\alpha\beta}\tilde{\psi}_\beta(t)=f_\alpha(t), \quad t>0 \ . \tag{2.10}$$

For continuous potentials, this approximation leads to a mean-field dynamics associated with the initial average forces in the nonequilibrium ensemble, and is applicable only for times small compared to a collision time. However, for hard spheres, the limit of infinitesimally small collision times has already been taken at the outset; consequently, Eq. (2.10) represents the dynamics for times *large* compared to a collision time. This interpretation is supported by the fact that $\Omega_{\alpha\beta}$ describes finite momentum transfer (collisions) for the case of hard spheres. These considerations are the primary motivation for studying models with such discontinuous and singular interactions—simple approximations include qualitative effects that would be more difficult to extract for continuous potentials. It should be noted that the short-time limit does not entail any limitations on density or space scale. Although this is an uncontrolled approximation, it is well known that related short-time hard-sphere limits (e.g., Enskog kinetic theory) predict surprisingly accurate long-time properties, such as transport coefficients,[4] at moderate densities and even qualitative accuracy at very high densities. A comparison of correlation functions calculated from Eq. (2.10) for the equilibrium state with those from a more accurate kinetic theory is given in Sec. III.

The autocorrelation of the fluctuating force $f_\alpha(t)$ is usually associated with the matrix $\gamma_{\alpha\beta}(t)$, which no longer appears in the approximate equation, (2.10). However, this association applies only for continuous potentials and must be modified for hard spheres. To identify the proper autocorrelation function for $f_\alpha(t)$, first note that Eq. (2.10) is local in time so that the forces are expected to be δ correlated in time (white noise),

$$\langle f_\alpha(t) f_\beta^*(0) \rangle = F_{\alpha\beta}\delta(t) \ . \tag{2.11}$$

It is shown in Appendix A that the definition of $f_\alpha(t)$ given by Eq. (2.8) leads to such a singular contribution, and the amplitudes $F_{\alpha\beta}$ can be identified as the coefficient of $\delta(t)$. There is also an additional nonsingular time dependence, but this should be neglected for self-consistency with the short-time limit. It is found that $F_{\alpha\beta}$ is simply related to $\Omega_{\alpha\beta}$ by

$$\Omega_{\alpha\sigma} w_{\sigma\beta} + w_{\alpha\sigma}\Omega^H_{\sigma\beta} = F_{\alpha\beta} \ , \tag{2.12}$$

where the superscript H denotes the Hermitian conjugate of the matrix. This relationship is the expected generalization of the corresponding equilibrium result for a wide class of Markov processes. It is proved in Appendix A directly from the microscopic definitions in (2.8). Identification of this nonequilibrium fluctuation-dissipation relation is one of the primary results of this section. The statistical properties of fluctuating forces are completely specified by the additional assumption that higher-order cumulants of $f_\alpha(t)$ are negligible. Then Eqs. (2.10) and (2.11) are the Langevin equations for a Gaussian-Markovian process.

To proceed, it is necessary to specify the choice of variables $\{\psi_\alpha\}$. Our primary interest here is in semimacroscopic properties of a sheared fluid. More precisely, the space and time scales of the phenomena to be studied are large compared to the characteristic mean free path and mean free time. As noted in the Introduction, such space scales can be comparable to, or even smaller than, atomic dimensions for a dense fluid. Still, these conditions represent the domain of "hydrodynamics." Here, the terminology hydrodynamics is used in a general sense to refer to the approximately closed dynamics of local conserved densities, and is not limited to the Navier-Stokes domain. For the chosen phenomena, therefore, it is appropriate to include among the variables $\{\psi_\alpha\}$ those corresponding to the local mass, energy, and momentum densities,

$$\begin{aligned} \tilde{z}_\alpha(\mathbf{k}) &= \sum_{n=1}^{N} c_\alpha(\mathbf{p}'_n)\phi_k(\mathbf{q}_n) \ , \\ c_\alpha(p_n) &\leftrightarrow (m, p_n^2/2m - \tfrac{3}{2}k_B T, \mathbf{p}_n \cdot \mathbf{e}^{(\alpha)}(k)) \ , \\ \phi_k(q_n) &\equiv e^{i\mathbf{k}\cdot\mathbf{q}_n}/[(2\pi)^3 V]^{1/2} \ . \end{aligned} \tag{2.13}$$

A Fourier representation has been chosen where the wave vector $\mathbf{k}$ takes on values appropriate to the chosen nonequilibrium boundary conditions (see Appendix A). The unit vectors $\mathbf{e}^{(\alpha)}$, for $\alpha = 3-5$, form a mutually orthogonal set with $\mathbf{e}^{(3)}$ along the $\mathbf{k}$ direction. Also, V is the volume and $\mathbf{p}'_n = \mathbf{p}_n - m\mathbf{U}(q_n)$ is the momentum of nth particle relative to the local average momentum associated with the flow field $\mathbf{U}(\mathbf{r})$. For uniform shear flow the latter has the form

$$U_i(\mathbf{r}) = U_{0i} + a_{ij} r_j, \quad a_{ij} = a\delta_{ix}\delta_{jy} \ . \tag{2.14}$$

The constant $\mathbf{U}_0$ can be eliminated by a suitable choice of coordinate system, and will be set equal to zero in the following. The coordinates of the shear rate tensor a_{ij} correspond to flow along the x axis with a constant gradient a along the y axis. Finally, the temperature in (2.13) is defined in terms of the average kinetic energy in the local rest frame of the flow,

$$\tfrac{3}{2} N k_B T = \left\langle \sum_{n=1}^{N} \frac{p'_n}{2m} \right\rangle^2 \ . \tag{2.15}$$

For hard spheres, there is no distinction between total and kinetic-energy densities.

In addition to the variables of Eq. (2.13), it is appropriate to include their bilinear combinations,

$$\begin{aligned} \tilde{b}_{\alpha\beta}(\mathbf{k},\mathbf{k}') \equiv{} & \tilde{z}_\alpha(\mathbf{k})\tilde{z}_\beta(\mathbf{k}') - \langle \tilde{z}_\alpha(\mathbf{k})\tilde{z}_\beta(\mathbf{k}') \rangle \\ & - \langle \tilde{z}_\alpha(\mathbf{k})\tilde{z}_\beta(\mathbf{k}')\tilde{z}^*_\sigma(\mathbf{k}_1) \rangle g^{-1}_{\sigma\nu}(\mathbf{k}_1,\mathbf{k}_2)\tilde{z}_\nu(\mathbf{k}_2) \ , \end{aligned} \tag{2.16}$$

$$g_{\alpha\beta}(\mathbf{k},\mathbf{k}') \equiv \langle \tilde{z}_\alpha(\mathbf{k})\tilde{z}^*_\beta(\mathbf{k}') \rangle \ . \tag{2.17}$$

The $\{\tilde{b}_{\alpha\beta}(\mathbf{k},\mathbf{k}')\}$ have been chosen to be symmetric, have zero average, and to be orthogonal to the set $\{\tilde{z}_\alpha\}$,

$$\langle \tilde{z}_\alpha(\mathbf{k})\tilde{b}_{\beta\sigma}(\mathbf{k}',\mathbf{k}'') \rangle = 0 \ . \tag{2.18}$$

The reason for including these variables is that they are expected to contribute on the same space and time scales as those for which the $\tilde{z}_\alpha(\mathbf{k})$ are important. In addition, they include a quantitatively different effect due to nonlinear mixing of the dynamics associated with the conserved densities (mode coupling). The Langevin equation for $\tilde{z}(\mathbf{k},t)$ now becomes.

$$\begin{aligned} \frac{\partial}{\partial t}\tilde{z}_\alpha(\mathbf{k};t) &+ \mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}')\tilde{z}_\beta(\mathbf{k}';t) \\ &+ N_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}',\mathbf{k}'')\tilde{b}_{\beta\gamma}(\mathbf{k}',\mathbf{k}'';t) = f_\alpha(\mathbf{k},t) \ , \end{aligned} \tag{2.19}$$

where the linear and bilinear couplings are defined by

$$\mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}')=-\langle [L_{+}\tilde{z}_{\alpha}(\mathbf{k})]\tilde{z}^{*}_{\sigma}(\mathbf{k}_1)\rangle g^{-1}_{\sigma\beta}(\mathbf{k}_1,\mathbf{k}') ,$$
$$N_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}',\mathbf{k}'')=-\tfrac{1}{2}\langle [L_{+}\tilde{z}_{\alpha}(\mathbf{k})]\tilde{b}^{*}_{\sigma\nu}(\mathbf{k}_1,\mathbf{k}_2)\rangle \times g^{-1}_{\sigma\beta}(\mathbf{k}_1,\mathbf{k})g^{-1}_{\nu\gamma}(\mathbf{k}_2,\mathbf{k}') \tag{2.20}$$

and the noise amplitude for this equation is

$$F_{\alpha\beta}(\mathbf{k},\mathbf{k}')=\mathcal{L}_{\alpha\sigma}(\mathbf{k},\mathbf{k}_1)g_{\sigma\beta}(\mathbf{k}_1,\mathbf{k}')+g_{\alpha\sigma}(\mathbf{k},\mathbf{k}_1)\mathcal{L}^{H}_{\sigma\beta}(\mathbf{k}_1,\mathbf{k}') . \tag{2.21}$$

Note that because of the condition (2.18), the nonlinear coupling $N_{\alpha\beta\gamma}$ does not contribute to $F_{\alpha\beta}$. To further simplify these results it is necessary to introduce the properties of the nonequilibrium ensemble, $\rho(\Gamma)$. For uniform shear flow, (2.14), it is possible to show that $\rho(\Gamma)$ is translationally invariant at constant $\{\mathbf{p}'_n\}$. Consequently, the matrices are diagonal in $\mathbf{k},\mathbf{k}'$,

$$g_{\alpha\beta}(\mathbf{k},\mathbf{k}')=\delta(\mathbf{k}-\mathbf{k}')g_{\alpha\beta}(\mathbf{k};a) ,$$
$$\mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}')=\left[-a_{ij}k_i\frac{\partial}{\partial k_j}\delta_{\alpha\beta}+M_{\alpha\beta}(\mathbf{k},a)\right]\delta(\mathbf{k}-\mathbf{k}') ,$$
$$F_{\alpha\beta}(\mathbf{k},\mathbf{k}')=\delta(\mathbf{k}-\mathbf{k}')F_{\alpha\beta}(\mathbf{k},a) . \tag{2.22}$$

The evaluation of $g_{\alpha\beta}(\mathbf{k};a)$, $M_{\alpha\beta}(\mathbf{k};a)$, and $F_{\alpha\beta}(\mathbf{k};a)$ is described in Appendix B. Although some elements can be calculated exactly; in general, further microscopic details of the stationary state are required. Two primary approximations are introduced in the calculations. First, the matrix elements are calculated only to first order in the shear rate. An appropriate dimensionless shear rate is $a^{*}\equiv at_0$ where t_0 is the Boltzman mean free time. At high densities t_0 is very small and $a^{*}<1$ even at the large shear rates used in computer simulations (some further qualifications of this estimate are given below). The second approximation is to neglect certain momentum correlations in the two- and three-particle reduced distribution functions, while preserving the exact spatial correlations. Although uncontrolled, the approximation is introduced in a manner that is consistent with stationarity in the single-particle phase space and the two-particle coordinate space. Further comments on this point are given in Sec. V.

The evaluation of the nonlinear coupling $N_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}',\mathbf{k}'-\mathbf{k})$ is discussed in the paper following this one. For the remainder of the discussion here attention is restricted to analysis of the linear Langevin equation.

III. CORRELATION FUNCTIONS

The dynamics of fluctuations around the stationary state is described by correlation functions for the variables $\{\tilde{z}_{\alpha}(\mathbf{k})\}$,

$$C_{\alpha\beta}(\mathbf{k},\mathbf{k}';t)=\langle \tilde{z}_{\alpha}(\mathbf{k},t)\tilde{z}^{*}_{\beta}(\mathbf{k}',t)\rangle . \tag{3.1}$$

The time dependence of $\tilde{z}_{\alpha}(\mathbf{k},t)$ is determined from the Langevin equation. Choosing the initial condition in the remote past ($t\rightarrow-\infty$) both $C_{\alpha\beta}(\mathbf{k},\mathbf{k}';t)$ and the equal time correlation functions,

$$C_{\alpha\beta}(\mathbf{k},\mathbf{k}',0)=g_{\alpha\beta}(\mathbf{k};a)\delta(\mathbf{k}-\mathbf{k}') \tag{3.2}$$

can be calculated self-consistently.

In this section we analyze the properties of the correlation function as determined by only the linear part of the Langevin equation. To clarify the meaning of such an approximation the full Langevin equation is first rewritten as

$$\left[\frac{\partial}{\partial t}-a_{ij}k_i\frac{\partial}{\partial k_j}\right]\tilde{z}_{\alpha}(\mathbf{k},t)+M_{\alpha\beta}(\mathbf{k};a)\tilde{z}_{\beta}(\mathbf{k},t)=h_{\alpha}(\mathbf{k}',t) \tag{3.3}$$

with the new "stochastic" variable

$$h_{\alpha}(\mathbf{k},t)\equiv f_{\alpha}(\mathbf{k},t)-N_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}',\mathbf{k}'')\tilde{b}_{\beta\gamma}(\mathbf{k},\mathbf{k}';t) . \tag{3.4}$$

The term $f_{\alpha}(\mathbf{k},t)$ gives a singular contribution to the correlation function for $h_{\alpha}(\mathbf{k},t)$ as indicated in Sec. II, so that

$$\langle h_{\alpha}(\mathbf{k},t)h^{*}_{\beta}(\mathbf{k}',0)\rangle=F_{\alpha\beta}(\mathbf{k},\mathbf{k}')\delta(t)+\Delta'_{\alpha\beta}(\mathbf{k},\mathbf{k}';t) . \tag{3.5}$$

The term $\Delta'_{\alpha\beta}(\mathbf{k},\mathbf{k}';t)$ is due to the second term in (3.4) and vanishes relative to the singular term as $t\rightarrow 0$. Also in this limit $h_{\alpha}(\mathbf{k},t)$ is orthogonal to $\tilde{z}_{\alpha}(\mathbf{k},t)$. Thus, formally setting the nonlinear terms of the Langevin equations to zero leads to the exact short-time Langevin equation in the space spanned by set $\{\tilde{z}_{\alpha}(\mathbf{k})\}$. Conversely, retaining the nonlinear terms gives the exact short-time Langevin equations in the larger space spanned by $\{\tilde{z}_{\alpha}(\mathbf{k}),\ \tilde{b}_{\alpha\beta}(\mathbf{k},\mathbf{k}')\}$. Evidently, increasing the dimension of the space in which the short-time dynamics is formulated is equivalent to retaining longer-time phenomena in the subspace $\{\tilde{z}_{\alpha}(\mathbf{k})\}$. For sufficiently short times $h_{\alpha}(\mathbf{k},t)$ is orthogonal to $\tilde{z}_{\beta}(\mathbf{k}')$ and the correlation function obeys the linear equation,

$$\left[\frac{\partial}{\partial t}-a_{ij}k_i\frac{\partial}{\partial k_j}\right]C_{\alpha\beta}(\mathbf{k},\mathbf{k}',t)+M_{\alpha\sigma}(\mathbf{k},a)C_{\sigma\beta}(\mathbf{k},\mathbf{k}';t)=0 . \tag{3.6}$$

The analysis of this equation is complicated by the differential operator with respect to $\mathbf{k}$. For small wave vectors a perturbation theory can be applied, as in Ref. 10. The qualitative effects of these convective terms are described in some detail there and are expected to be similar for the larger wave-vector case considered here. For example, the correlation functions are nondiagonal in $\mathbf{k},\mathbf{k}'$ at finite t and have faster than exponential decay. Also, there is a distortion of the static structure factor $[g_{11}(\mathbf{k};a)]$ due to this convective term. This effect has been studied by Hess and co-workers[15,16] using a simple Schmoluchowsky equation for $g_{11}(\mathbf{k};a)$ with a single relaxation time approximation, leading to good agreement with computer simulation results. Here we will focus instead on the effects due to wave vectors along the gradient, $\mathbf{k}=k\hat{y}$. In this case the convective terms vanish, so we are looking at a more subtle reflection of the shear flow. For example, some contributions are due to changes in the transport coefficients due to the shear.

For this choice of wave vector, the correlation function is found to be (see Ref. 10 for details)

$$C_{\alpha\beta}(\mathbf{k},\mathbf{k}';t)=\delta(\mathbf{k}-\mathbf{k}')C_{\alpha\beta}(\mathbf{k},t)\ ,$$

$$C_{\alpha\beta}(\mathbf{k};t)=\sum_{p=1}^{5} e^{-\lambda_p(\mathbf{k};a)t}\xi_\alpha^{(p)}(\mathbf{k};a)\eta_\sigma^{(p)}(\mathbf{k};a)g_{\sigma\beta}(\mathbf{k};a)\ . \quad (3.7)$$

Here $\lambda_p(\mathbf{k};a)$, $\xi_\beta^{(p)}(\mathbf{k};a)$, and $\xi_\beta^{(p)}(\mathbf{k};a)$ are the eigenvalues and eigenfunctions of $M_{\alpha\beta}(\mathbf{k};a)$,

$$M_{\alpha\beta}(\mathbf{k};a)\xi_\beta^{(p)}(\mathbf{k};a)=\lambda_p(\mathbf{k};a)\xi_\alpha^{(p)}(\mathbf{k};a)\ . \quad (3.8)$$

Also, $\eta_\alpha^{(p)}(\mathbf{k};a)$ is the associated biorthogonal set of vectors.

These eigenfunctions and eigenvalues define the hydrodynamic modes for decay of fluctuations away from the state of uniform shear flow. Consider first the case of zero shear rate and small wave vector and assume *both* $kl_0 \ll 1$ and $k\sigma \ll 1$, where l_0 is the mean free path and σ is the hard-sphere diameter. Then the eigenvalues are simply those associated with the linearized Navier-Stokes hydrodynamic equations,

$$\lambda_1=\lambda_2^*=-ick+\tfrac{1}{2}\Gamma k^2,\quad \lambda_3=Dk^2,\quad \lambda_4=\lambda_5=\nu k^2\ . \quad (3.9)$$

Here c is the sound speed, Γ is the sound damping constant, D is the thermal diffusivity, and ν is the kinematic viscosity. The first two eigenvalues represent damped sound modes, the second represents heat diffusion, and the last two represent twofold degenerate shear diffusion. Such hydrodynamic excitations are expected to exist more generally whenever kl_0 is sufficiently small, even if $k\sigma$ is large. The latter characterizes wavelengths for which the fluid structure can be important. At very high densities, the mean free path becomes very small as the particles are more closely packed. Figure 1 shows the line of $kl_0=0.5$ in the $k^*\equiv k\sigma$ versus $n^*\equiv n\sigma^3$ plane, so the hydrodynamic modes are relevant below this line. However, at densities above about 0.7 the hydrodynamic domain includes $k\sigma>1$. The hydrodynamic modes are then affected significantly by the atomic structure. Such short-wavelength hydrodynamics have been investigated extensively by de Schepper and Cohen for zero shear rate using an Enskog kinetic equation.[3] Figures 2 and 3 compare the results obtained from Eq. (3.8) at $a^*=0$ with those of de Schepper and Cohen. The results are seen to be qualitatively quite similar. Quantitative differences can be traced partly to different values of the thermal conductivity and shear viscosity in the two models. Several features are of particular interest. First, the degeneracy of the shear modes is maintained due to a decoupling of the longitudinal and transverse momentum components at all wave vectors. At sufficiently large wave vectors the sound velocity vanishes over some range and two distinct purely damped modes replace the propagating sound modes. The eigenvalues are all significantly softened relative to an extrapolation of their Navier-Stokes form to large wave vectors. Of particular interest is the heat mode whose eigenvalue is very small for $k^*=6.5$ (near the peak of the structure factor). This implies a slowly decaying excitation for wavelengths of the order of the particle size. Finally, it is noted that the complex eigenvalues always occur as complex conjugate pairs. The density autocorrelation function calculated from Eq. (3.7) at zero shear rate also compares favorably with computer simulation results[4] (Fig. 4). The quantitative discrepancies at longer times is due to the differences in the heat mode eigenvalue shown in Figs. 2 and 3. These comparisons with kinetic theory and computer simulation at zero shear rate are included here to show that the approximations leading to the hydrodynamic model preserve the qualitative features of dense fluid dynamics even at large wave vectors.

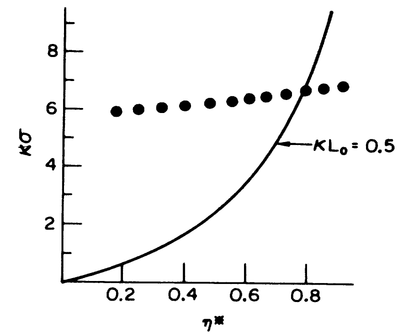

FIG. 1. Relationship of k^* to kl_0 as a function of density, for hard spheres. The solid line is $kl_0=0.5$ so hydrodynamics applies below this line. Also shown is the position for the first peak of the static structure factor ($\cdots$).

Now consider the effect of a finite shear rate. The case of $a^*=0.02$ is shown in Figs. 5 and 6. The degeneracy of the shear modes is broken due to a coupling of longitudinal and transverse momentum components by the shear-

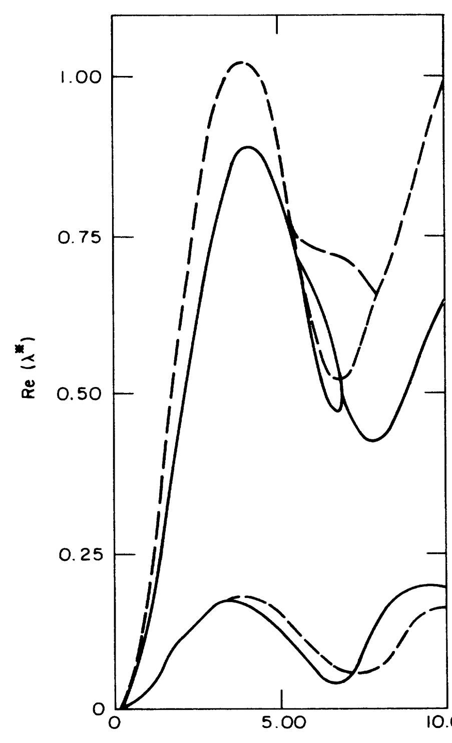

FIG. 2. Real parts of the eigenvalues at $a^*=0$ and $n^*=0.88$; —— from Eq. (3.8), and — — — from Ref. 3.

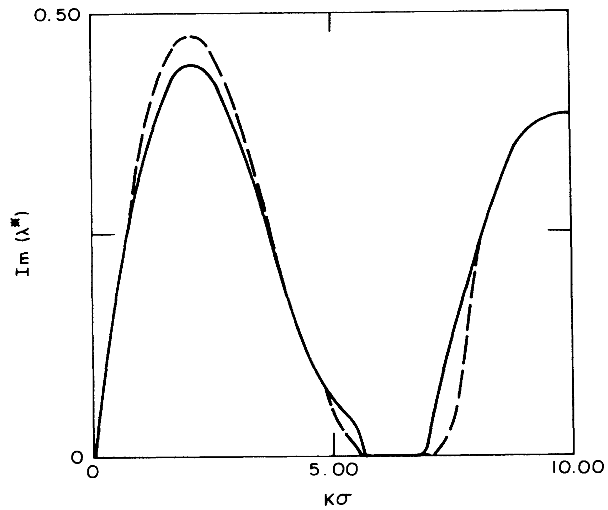

FIG. 3. Same as Fig. 1 for the imaginary parts of the eigenvalues.

rate tensor. One of the shear modes is unchanged from its value at zero shear rate and is not shown. The other four modes behave qualitatively as follows. For small k^* there are four propagating modes, the two sound modes plus two new modes replacing the heat mode and one shear mode. At larger k^* the two sound modes persist, but the heat and shear modes reappear as purely damped modes. At about $k^*=5.7$ the sound velocity vanishes, as in the zero shear rate case, to give four damped modes. Finally, the shear mode becomes propagating again above $k^* \sim 7.2$.

The results for larger shear rates are similar. The real parts of the eigenvalues are shown in Figs. 7 and 8 for $a^*=0.04$ and 0.06. The main trend to notice is that the range of k^* for which the heat mode occurs as a propagating mode increases with a^*. The large wave-vector hydrodynamics for the decay of deviations from the nonequilibrium steady state of shear flow is therefore quite unusual. In the region of four propagating modes, ordinary heat diffusion becomes propagating with a velocity proportional to the shear rate. Typically the sound modes at large wave vector are strongly damped but this new pair of propagating heat modes has a much longer lifetime. These effects are most pronounced for the chosen direction of **k** along the velocity gradient, while the zero shear rate results are regained for **k** orthogonal to both the flow and the gradient.

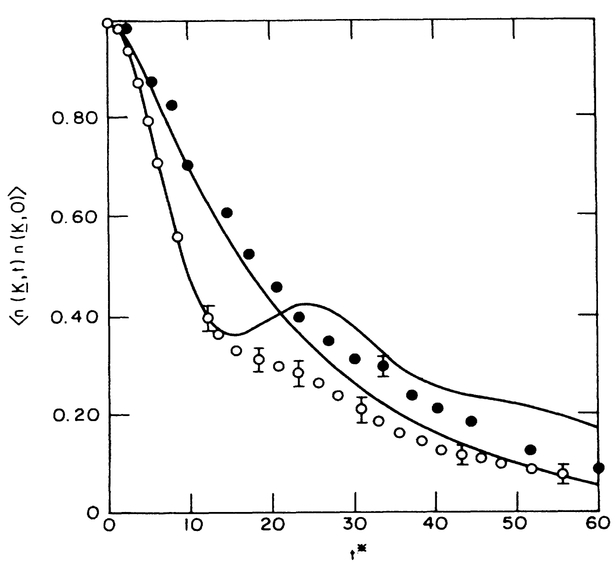

FIG. 4. Density autocorrelation function at $n^*=0.88$ for $k^*=0.76$ and 6.83; —— from Eq. (3.7), and ●, molecular dynamics, Ref. 14.

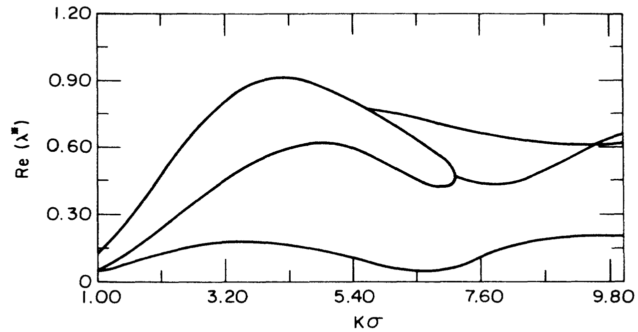

FIG. 5. Same as Fig. 2 at $a^*=0.020$.

The correlation functions can be calculated from the known eigenvalues and eigenfunctions using Eq. (3.7) and the noise amplitude $F_{\alpha\beta}$ calculated to first order in a^*. The structure factor (equal time-density autocorrelation function) is shown in Fig. 9 for a range of shear rates. The peak of the structure factor decreases with increasing shear rate, and broadens slightly. This decrease of correlations under shear has been obtained from simple models[15] for other **k** directions and observed in both computer simulations[16] and light scattering from sheared colloidal suspensions.[17] From symmetry considerations it can be shown that the first corrections to the equilibrium structure factor are of order a^2; thus the Langevin equation is being used here to "bootstrap" first-order perturbation theory input to estimate these second-order effects. The time-dependent density autocorrelation function is also easily evaluated from Eq. (3.7). In general, the density fluctuations couple to both the two sound and the two "heat-shear" modes at finite shear rate. However, as the shear is increased the coupling to the heat modes increases at the expense of the sound modes. This is illustrated in Fig. 10, showing the dynamic structure factor

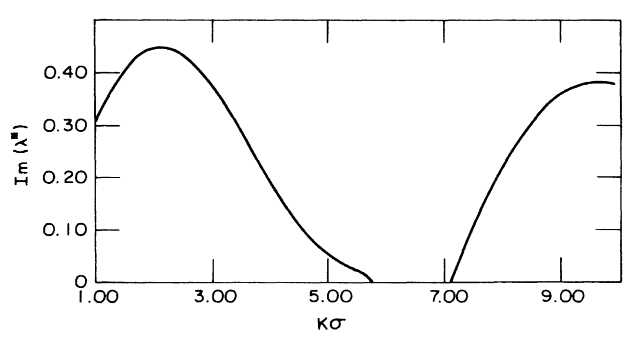

FIG. 6. Same as Fig. 3 at $a^*=0.020$.

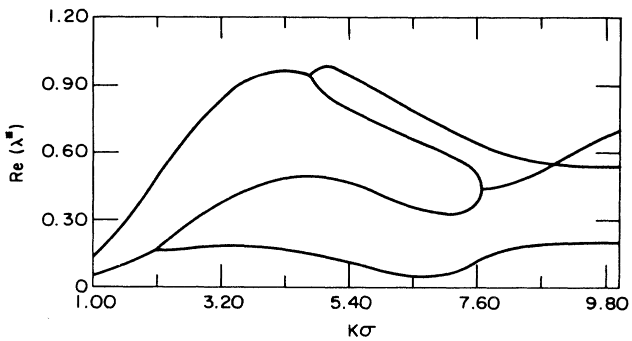

FIG. 7. Same as Fig. 2 at $a^* = 0.041$.

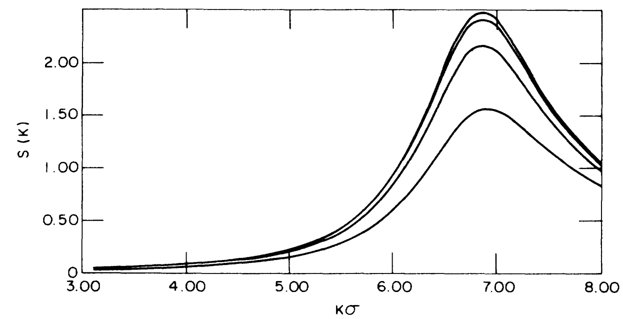

FIG. 9. Static structure factor for $k_x = k_z = 0$ at $a^* = 0$, 0.021, 0.041, and 0.061. The peak decreases and broadens as the shear rate increases.

[Fourier-transformed density autocorrelation function, $S(k,w)$] as a function of frequency for $k^* = 0.5$. Since the heat mode is propagating, $S(k,w)$ is the superposition of four Lorentzians. The velocity of propagation for the heat modes is small, so there is a qualitative similarity with the zero shear rate result. As the shear rate increases the sound peak diminishes, representing a more dominant coupling of the density to the heat mode eigenvector. Near the minimum of the heat mode eigenvalue, $k^* = 6.5$, the heat mode represents primarily a density excitation.

IV. INSTABILITY

An advantage of the nonequilibrium computer simulation methods is the ability to study non-Newtonian effects in simple atomic fluids. An usual and unexpected effect was observed by Erpenbeck in one such study for hard spheres.[11] A rapid decrease in the shear viscosity with increasing shear rate was found over a narrow range. On the large shear rate side the particles were observed to be localized into a hexagonally packed array of tubes along the direction of flow (Fig. 11). This transition to an ordered fluid is difficult to understand for such simple, structureless particles. Subsequently, the phenomenon of ordering at large shear rates has been observed for other interatomic potentials as well.[18]

It has been suggested that this disorder-order transition can be understood as a nonequilibrium distortion of the equilibrium freezing transition.[19] The basic idea is that a nonequilibrium free energy can be identified which depends on the shear rate. This generalized thermodynamic function could reflect a distortion of the equilibrium freezing as an ordering in the nonequilibrium fluid. While the idea is appealing, its theoretical basis has not yet been developed. Alternatively, Kirkpatrick and Nieuwoudt[13] and the present authors[12] have suggested that the transition may be due to a hydrodynamic instability. This might seem unlikely at first, since planar Couette flow is known to be very stable at the low Reynolds numbers used in computer simulations. However, the system size is small in the simulations and the stability analysis requires a short-wavelength hydrodynamics such as that considered here.

The possibility of such an instability at short wavelengths is suggested by the soft heat mode already present at zero shear rate. If there is some additional mechanism from the nonequilibrium state to further soften the heat mode until it vanishes at some wave vector, an instability results. To indicate that this is probably the case the results of Eq. (3.8) are extended to larger shear rates in Fig. 12, at $n^* = 0.88$. Only the real part of the heat mode is shown. At $a^* = 0.1$ the results are very close to those at $a^* = 0.06$ in Fig. 8, although the mode is now propagating in the range of k^* shown. As the shear rate is increased the minimum decreases until it vanishes at about $a^* = 0.13$. The critical wave vector for this instability is about $k^* = 6$.

The above calculations are for the wave vector along the velocity gradient. Other directions lead to a larger critical shear rate, so the instability is associated with density fluctuations along the direction of the gradient. This is in qualitative agreement with the observations from computer simulations: first, a layering into planes

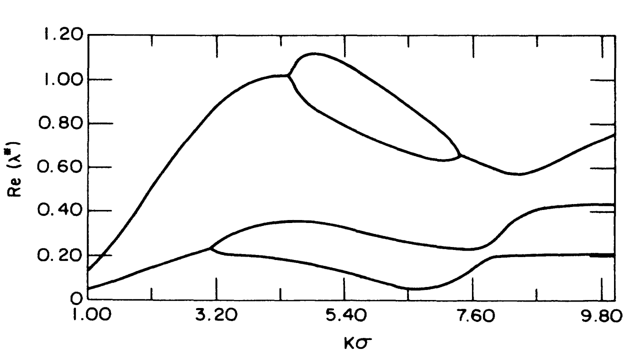

FIG. 8. Same as Fig. 2 at $a^* = 0.061$.

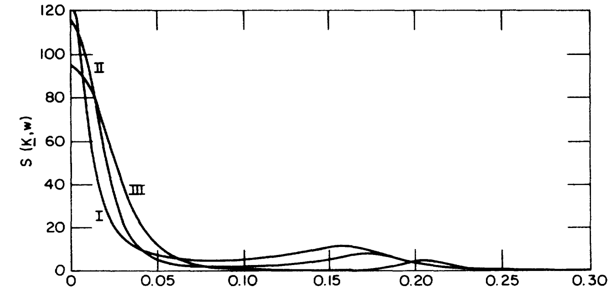

FIG. 10. Dynamic structure factor at $k^* = 0.5$ as a function of frequency for $a^* = 0$, 0.041, and 0.081 (I, II, and III, respectively).

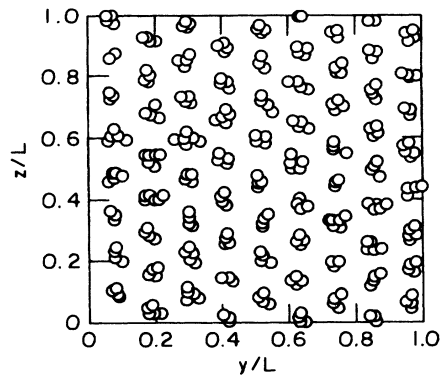

FIG. 11. Illustration of the ordered fluid phase (from Ref. 11).

orthogonal to the gradient occurs, followed by the formation of tubes within the planes. Figure 13 shows that there is also a qualitative agreement with the density dependence of the critical shear rate.

Since these calculations are based on a model that is valid only to first order in a^*, the results are not expected to be quantitatively reliable at the large shear rates for which the instability occurs. An indication that the perturbation theory fails at large shear rates is given by the noise matrix, $F_{\alpha\beta}$. At shear rates above $a^*=0.07$, one of its eigenvalues becomes negative over some range of the wave vectors considered here. This unphysical property is perhaps not too surprising since some of the input to the calculation is questionable at that point. For example, the first Chapman-Enskog approximation for the distribution function, Eq. (B21), leads to negative values for velocities greater than about twice the thermal velocity. This also casts some doubt on the validity of the eigenvalues of $M_{\alpha\beta}$ and the resulting instability, as well at these large shear rates. However, we believe the instability is real, in spite of the problems with the noise matrix. To support this belief, the second term in (B21) was set equal to zero so that a positive distribution function is assured (this amounts to a local equilibrium approximation). It is found that the instability still occurs, although at a slightly larger critical shear rate, but now in a range of wave vectors for which the noise matrix is positive. To provide a proper theoretical description some account must be

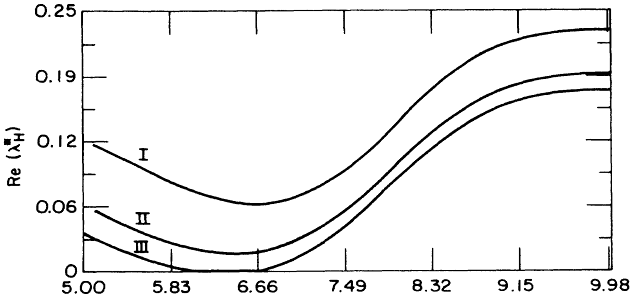

FIG. 12. The real part of the propagating heat mode for $a^*=0.10$, 0.12, and 0.13 (I, II, and III, respectively).

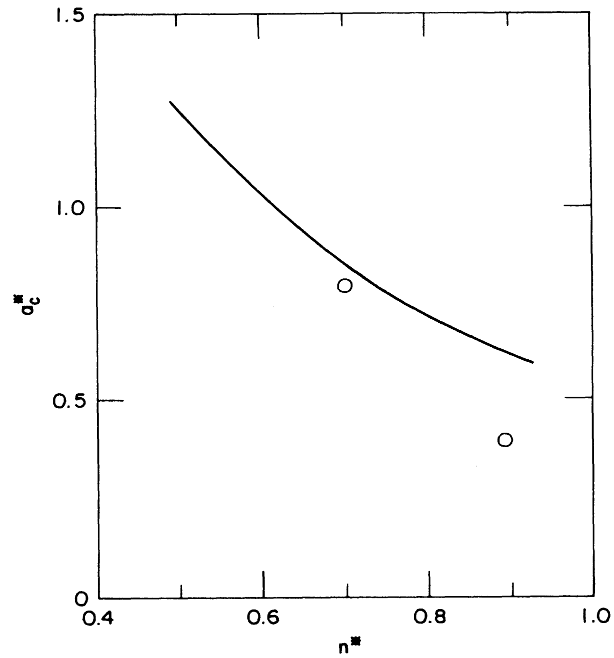

FIG. 13. Density dependence of the critical shear rate, a_c^*, ——; and from molecular dynamics, ○.

taken of the higher-order shear rate dependence. At the highest densities, it turns out that the contributions from the local equilibrium distribution in Eq. (B21) are almost an order of magnitude greater than the others. It appears possible to extend the present calculations to include these effects. Also, the input data for the hard sphere structure may need to be improved beyond the Percus-Yevick approximation at the highest densities considered here.

The analysis of Kirkpatrick and Nieuwoudt is similar in spirit to that given here. They consider an approximate set of hydrodynamic equations for the density and momentum that are expected to be valid near the peak of the structure factor. Their equations are obtained from an Enskog kinetic equation, calculated to second order in the shear rate. This kinetic theory assumes a local equilibrium state in the collisional process and therefore neglects momentum correlations in the two-particle phase space, as is done here. They estimate contributions from the three-particle distribution function using a Kirkwood superposition approximation. They find an instability for k^* along the velocity gradient due to a coupling between the longitudinal momentum and the density at second order in a^*. This is in contrast to the results here that are due to a coupling of the longitudinal momentum to a transverse momentum component at first order in a^*. In our calculations we have explicitly imposed the conditions of stationarity, and this seems to be the reason we find an instability at first order. It is likely that both types of coupling occur at second order in the shear rate but it is not clear which one is dominant. Both studies must be considered as tentative identifications of a hydrodynamic instability underlying the Erpenbeck disorder-order transition.

V. DISCUSSION

A set of stochastic nonlinear differential equations has been derived describing fluctuations of the conserved densities of a simple fluid about a state of uniform shear flow. Beginning with the exact, microscopic Liouville equation, a projection operator formalism was used to separate the slowly decaying "hydrodynamic" (i.e., conserved density) modes from the more quickly varying microscopic modes. Taking the exact short-time limit and assuming that the inhomogeneous "noise" obeys a Gaussian distribution, a set of equations having the familiar form of phenomenological Langevin equations was derived. This derivation, which begins at the microscopic level, allows us to go beyond the usual phenomenological equations to include a description of atomic length scale fluctuations which, in equilibrium, agrees well with computer simulation and kinetic theory.

These equations were then linearized and the resulting linear modes examined in some detail. As shown previously, the convective term gives rise to the rapid decay of all modes except those confined to a plane perpendicular to the flow ($k_x=0$). Only these modes have been considered here. The most striking feature of these modes at low shear rates is the combination of the heat mode and a shear mode to form a new pair of propagating modes at large wave vector. At larger shear rates, the heat mode was found to be softened to the point of becoming unstable. It is suggested that this linear instability is the reason for the order-disorder transitions seen at similar shear rates in computer simulations of shear flow.

It should be pointed out that the instability we find is at short wavelengths that correspond to the first peak of the static structure factor. It is the short-time properties of the dense fluids at high shear rates that make the density mode unstable in the direction of the velocity gradient. Thus the instability is present even in the linear theory. The long-time memory effects coming from the nonlinear mode-coupling terms are expected to affect the results in a qualitative way, i.e., the critical shear rate might be changed in a renormalized theory. Thus the results given here regarding the hydrodynamic instability are only qualitative and cannot be compared quantitatively to the results of the simulations. It would seem, however, that the observation of the new propagating modes at smaller shear rates in computer simulations would be a practical check of the present model in a regime where both the model and the simulations are most trustworthy.

ACKNOWLEDGMENTS

This research was supported by National Science Foundation Grant No. CHE 8411932. One of the authors, J.F.L., received support from the U. S. Department of Energy, Basic Energy Sciences, Materials Sciences, under Contract No. W-31-109-ENG-38.

APPENDIX A

In this appendix some results used in the derivation of the hard-sphere nonequilibrium Langevin equation are given. The generators of the hard-sphere dynamics in Eq. (2.1) are defined by

$$L_{\pm}=L_0\pm\tfrac{1}{2}\sum_{n\neq m}\sum T_{\pm}(n,m)\ , \tag{A1}$$

with

$$L_0\equiv\sum_{n=1}^{N}\mathbf{v}_n\cdot\nabla_{q_n}+L_{\text{ext}}\ ,$$
$$T_{\pm}(n,m)\equiv\sigma^2\int d\hat{\sigma}\,|\mathbf{g}\cdot\hat{\sigma}|\Theta(\mp\mathbf{g}\cdot\hat{\sigma})\delta(\mathbf{r}_{nm}-\boldsymbol{\sigma})(b_\sigma-1)\ . \tag{A2}$$

Here, $\mathbf{g}=\mathbf{v}_n-\mathbf{v}_m$ is the relative velocity, $\mathbf{r}_{nm}=\mathbf{r}_n-\mathbf{r}_m$ is the relative position, and Θ is the Heaviside step function restricting the integration to either the forward or backward hemisphere of the angular integration $d\hat{\sigma}$. Also, σ is the hard-sphere diameter and b is the operator changing the velocities of the pair (n,m) to their scattered velocities,

$$b_\sigma\mathbf{v}_n=\mathbf{v}_n-\hat{\sigma}(\hat{\sigma}'\cdot\mathbf{g}),\quad b_\sigma\mathbf{v}_m=\mathbf{v}_m+\hat{\sigma}(\hat{\sigma}'\cdot\mathbf{g})\ . \tag{A3}$$

The operator, L_{ext}, in Eq. (A1) represents external nonconservative forces required to maintain the steady state. In addition, the operators $L_{\pm}$ must be supplemented with boundary conditions. For the case of uniform shear flow discussed here, these are the Lees-Edwards boundary conditions. In their simplest form these are periodic boundary conditions on both the position and momentum of all particles in the local Lagrangian frame of the macroscopic flow,

$$\mathbf{p}_n'=\mathbf{p}_n-m\mathbf{U}(\mathbf{q}_n)\ ,$$
$$\mathbf{q}_n'=\mathbf{q}_n-\mathbf{U}(\mathbf{q}_n)t\ , \tag{A4}$$

where $\mathbf{U}(\mathbf{r})$ is the flow velocity defined in Eq. (2.14). Then, for example, a variable such as those in (2.13) has a Fourier representation and the periodic boundary conditions require

$$e^{i\mathbf{k}\cdot\mathbf{q}_n}=e^{i\boldsymbol{\kappa}\cdot\mathbf{q}_n'}=e^{i\boldsymbol{\kappa}\cdot(\mathbf{q}_n'+2L\hat{y})}\ , \tag{A5}$$

where $2L$ is the distance between the y boundaries and $\boldsymbol{\kappa}$ is determined from (A4) to be

$$\kappa_i=k_i+k_ja_{ji}t=n\pi/2L\ . \tag{A6}$$

The periodic boundary conditions in the Lagrangian frame imply that $\boldsymbol{\kappa}$ is constant, or equivalently that $\mathbf{k}$ depends on time. The Langevin equations of the main text therefore must be understood as having a time derivative at constant $\mathbf{k}$.

The Lees-Edwards boundary conditions lead to an exact solution to the macroscopic conservation laws, with the velocity fields given by Eqs. (2.14) and (2.15), constant density, and a temperature determined from

$$\tfrac{3}{2}nk_B\frac{\partial T}{\partial t}=-a_{ij}P_{ij}+\langle L_{\text{ext}}K'\rangle\ , \tag{A7}$$

where P_{ij} is the macroscopic pressure tensor and K' is the kinetic energy in the local rest frame. Without the external forces, Eq. (A7) determines the viscous heating due to the shear generated by the boundary conditions. It is convenient to consider instead a truly stationary state by introducing external nonconservative forces to compensate for viscous heating,

$$L_{\rm ext}=\sum_{n=1}^{N}\mathbf{F}_{\rm ext}(\mathbf{p}_n')\cdot\nabla_{p_n'}\ , \tag{A8}$$

$$\mathbf{F}_{\rm ext}(n)=-\gamma\mathbf{p}_n'\ . \tag{A9}$$

The parameter γ can be fixed by the requirement $\partial T/\partial t=0$. Actually, a stronger condition is used in computer simulations of shear flow,

$$\frac{dK'}{dt}=0\ . \tag{A10}$$

In this case γ becomes a phase function,

$$\begin{aligned}&\gamma=-(2K')^{-1}a_{ij}T_{ij}'\ ,\\&T_{ij}'=\sum_{n=1}^{N}\frac{p_{ni}'p_{nj}'}{m}+m\hat\sigma^3\sum_{n\neq m}\sum\int d\hat\sigma\,\Theta(-\hat\sigma\cdot\mathbf{g})|\mathbf{g}\cdot\boldsymbol{\sigma}|\hat\sigma_i\hat\sigma_j(\hat\sigma\cdot\mathbf{g})\delta(\mathbf{r}_{nm}-\hat\sigma)\ .\end{aligned} \tag{A11}$$

It is useful to define an adjoint operator $-\bar L_-$ associated with L_+ by

$$\int d\Gamma\,\rho(\Gamma)L_+A(\Gamma)\equiv-\int d\Gamma[\bar L_-\rho(\Gamma)]A(\Gamma) \tag{A12}$$

for arbitrary phase functions A. Then it is easily found that $\bar L_-$ is given by

$$\bar L_-=L_0-\tfrac{1}{2}\sum_{n\neq m}\sum\bar T_-(n,m)+\sum_n[\nabla_{p_n}\cdot\mathbf{F}_{\rm ext}(\mathbf{p}_n')]\ ,$$

$$\bar T_-(n,m)=\sigma^2\int d\hat\sigma|\mathbf{g}\cdot\hat\sigma|\Theta(\mathbf{g}\cdot\boldsymbol{\sigma})\times[\delta(\mathbf{r}_{nm}-\boldsymbol{\sigma})b_\sigma-\delta(\mathbf{r}_{nm}+\boldsymbol{\sigma})]\ . \tag{A13}$$

Using this definition, the correlation function for the fluctuating forces f_α can be calculated from Eq. (2.8) in the form

$$\begin{aligned}\langle f_\alpha(t)f_\beta^*\rangle&=\langle[Qe^{L't}QL_+\tilde\psi_\alpha][QL_+\tilde\psi_\beta]^*\rangle\\&=-\langle\rho^{-1}[\bar L_-\rho Qe^{L't}QL_+\tilde\psi_\alpha]\tilde\psi_\beta^*\rangle\ .\end{aligned} \tag{A14}$$

For discontinuous potentials such as hard spheres there is a singular part of the force correlation function, so it can be written as

$$\langle f_\alpha(t)f_\beta^*\rangle=F_{\alpha\beta}\delta(t)+\Delta_{\alpha\beta}(t)\ . \tag{A15}$$

By definition, $\Delta_{\alpha\beta}(t)$ is regular as $t\to0+$, so for the short-time Langevin equation it is sufficient to identity only $F_{\alpha\beta}$. For hard spheres this term arises from products of two binary collision operators $\bar T_-(n,n')$ and $T_+(n,n')$ for the same pair of particles.[20] Further details will not be given here, but the relevant part of (A15) is found to be

$$F_{\alpha\beta}\delta(t)=\lim_{t\to0+}\tfrac{1}{2}\sum_{n,n'}\int d\Gamma\tilde\psi_\beta^*\bar T_-(n,n')\rho e^{L_0t}T_+(n,n')\tilde\psi_\alpha\ . \tag{A16}$$

Use of the explicit forms for $\bar T_-(n,n')$ and $T_+(n,n')$ in (A16) leads to the result

$$\begin{aligned}F_{\alpha\beta}\delta(t)&=-\tfrac{1}{2}\sum_{n,n'}\int d\Gamma\,\tilde\psi_\beta^*[\rho T_+(n,n')\tilde\psi_\alpha+\bar T_-(n,n')\rho\tilde\psi_\alpha-\tilde\psi_\alpha\bar T_-(n,n')\rho]\\&=-\int d\Gamma\,\tilde\psi_\beta^*[\rho L_+\tilde\psi_\alpha-\bar L_-(\rho\tilde\psi_\alpha)+\tilde\psi_\alpha(\bar L_-\rho)]\\&=-\langle[L_+\tilde\psi_\alpha]\tilde\psi_\beta^*\rangle-\langle[L_+\tilde\psi_\beta]^*\tilde\psi_\alpha\rangle+\langle[L_+(\tilde\psi_\alpha\tilde\psi_\beta^*)]\rangle\ .\end{aligned} \tag{A17}$$

The last term can be written as the initial time derivative of the equal time correlation function, $w_{\alpha\beta}$, at $t=0^+$. Then with Eq. (2.8) this is recognized as

$$F_{\alpha\beta}=\Omega_{\alpha\sigma}w_{\sigma\beta}+w_{\alpha\sigma}\Omega_{\sigma\beta}^H+\frac{\partial}{\partial t}w_{\alpha\beta}\ . \tag{A18}$$

For stationary states the last term on the right vanishes, leaving Eq. (2.12) of the text.

APPENDIX B: EVALUATION OF $g_{\alpha\beta}(\mathbf{k};a)$, $M_{\alpha\beta}(\mathbf{k};a)$, AND $F_{\alpha\beta}(\mathbf{k};a)$

As indicated at the end of Sec. II the matrices $g_{\alpha\beta}$, $M_{\alpha\beta}$, and $F_{\alpha\beta}$ are calculated only to first order in the shear rate. To this order the contributions from the external force, applied to maintain the constant temperature, vanish. A typical term is

$$\langle L_{\rm ext}\tilde{z}_\alpha(\mathbf{k})\tilde{z}^*_\beta(\mathbf{k}')\rangle=\langle[L_{\rm ext}\tilde{z}_\alpha(\mathbf{k})]\tilde{z}^*_\beta(\mathbf{k}')\rangle+\langle\tilde{z}_\alpha(\mathbf{k})[L_{\rm ext}\tilde{z}^*_\beta(\mathbf{k}')]\rangle\ . \tag{B1}$$

It is sufficient to consider only the first term on the right-hand side. Using the explicit form of $L_{\rm ext}$ given by Eq. (2.8) leads directly to

$$\begin{aligned}
&\langle[L_{\rm ext}\tilde{z}_1(\mathbf{k})]\tilde{z}^*_\alpha(\mathbf{k}')\rangle=0\ ,\\
&\langle[L_{\rm ext}\tilde{z}_2(\mathbf{k})]\tilde{z}^*_\sigma(\mathbf{k}')\rangle=-\langle\gamma[\tilde{z}_2(\mathbf{k})+\tfrac{3}{2}k_BT\tilde{z}_1(\mathbf{k})]\tilde{z}^*_\sigma(\mathbf{k}')\rangle\ ,\\
&\langle[L_{\rm ext}\tilde{z}_\alpha(\mathbf{k})]\tilde{z}^*_\beta(\mathbf{k}')\rangle=-\langle\gamma\tilde{z}_\alpha(\mathbf{k})\tilde{z}^*_\sigma(\mathbf{k}')\rangle,\quad \alpha=3\text{–}5\ .
\end{aligned} \tag{B2}$$

According to Eq. (A11), γ is of the first order in the shear rate and the nonequilibrium ensemble average in (B2) can be replaced by the Gibbs ensemble. Then Eq. (B2) can be expressed as

$$\langle[L_{\rm ext}\tilde{z}_\alpha(\mathbf{k})]\tilde{z}^*_\beta(\mathbf{k}')\rangle\to-a\langle(K)^{-1}A_{\alpha\beta};\beta\rangle\ , \tag{B3}$$

where $A_{\alpha\sigma}$ is a sum of phase functions whose momentum dependence scales as a power, and the brackets $\langle\ ;\beta\rangle$ denote an equilibrium average at temperature $T=(k_B\beta)^{-1}$. The following identity can be used for a hard-sphere fluid. Let A be one of the contributions to $A_{\alpha\beta}$ whose momentum dependence scales with the power p. Then

$$\begin{aligned}
\langle K^{-1}A;\beta\rangle&=\int_0^\infty d\lambda\langle Ae^{-\lambda K};\beta\rangle=\int_0^\infty d\lambda\left[\frac{\beta}{\beta+\lambda}\right]^{3N/2}\langle A;\beta+\lambda\rangle\\
&=\int_0^\infty d\lambda\frac{\beta^{3N}}{(\beta+\lambda)^{(3N+p)/2}}\langle A;1\rangle=\beta^{3N/2}\langle A;1\rangle\int_\beta^\infty\frac{d\lambda}{\lambda^{(3N+p)/2}}\\
&=\frac{2}{(3N+p-2)\beta^{3p/2}}\langle A;\beta\rangle\ ,
\end{aligned} \tag{B4}$$

where N is the number of particles. This result, applied to Eq. (B2) shows that the contribution from the external forces is of relative order N^{-1} and may be neglected.

Next, the "fluctuation-dissipation relation" (A18) can be simplified using the stationarity condition

$$\langle L_+\tilde{z}_\alpha(\mathbf{k})\tilde{z}^*_\beta(\mathbf{k}')\rangle=-\langle(\rho^{-1}\bar{L}_-\rho)\tilde{z}_\alpha(\mathbf{k})\tilde{z}^*_\beta(\mathbf{k}')\rangle=0 \tag{B5}$$

to obtain Eq. (2.21)

$$F_{\alpha\beta}(\mathbf{k},\mathbf{k}')=\mathcal{L}_{\alpha\sigma}(\mathbf{k},\mathbf{k}'')g_{\sigma\beta}(\mathbf{k}'',\mathbf{k}')+g_{\alpha\sigma}(\mathbf{k},\mathbf{k}'')\mathcal{L}^H_{\sigma\beta}(\mathbf{k}'',\mathbf{k}')\ . \tag{B6}$$

The linear operator $\mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}')$ is defined by Eq. (2.20),

$$\mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}')\equiv-\langle[L_+\tilde{z}_\alpha(\mathbf{k})]\tilde{z}^*_\sigma(\mathbf{k}')\rangle g^{-1}_{\sigma\beta}(\mathbf{k}',\mathbf{k})\ . \tag{B7}$$

To establish the diagonal form given in Eq. (2.22) the definitions (2.13) for $\tilde{z}_\alpha(\mathbf{k})$ can be used to calculate directly,

$$\begin{aligned}
L_+\tilde{z}_\alpha(\mathbf{k})&=\left[\sum_n\frac{\mathbf{p}_n}{m}\cdot\nabla_{q_n}+L_{\rm ext}+L_I\right]\tilde{z}_\alpha(\mathbf{k})\\
&=a_{ij}\left[k_i\frac{\partial}{\partial k_j}\delta_{\alpha\beta}-e_i^{(\alpha)}e_j^{(\beta)}+e_m^{(\alpha)}k_i\frac{\partial e_m^{(\beta)}}{\partial k_j}\right]\tilde{z}_\beta(\mathbf{k})\\
&\quad+\sum_n\phi_k(\mathbf{q}_n)m^{-1}[c_\alpha(p_n')i\mathbf{k}\cdot\mathbf{p}_n'-\delta_{\alpha2}a_{ij}p_{ni}'p_{nj}']+L_{\rm ext}\tilde{z}_\alpha(\mathbf{k})+L_I\tilde{z}_\alpha(\mathbf{k})\\
&\equiv a_{ij}k_i\frac{\partial}{\partial k_j}z_\alpha(\mathbf{k})+X_\alpha(\mathbf{k})\ .
\end{aligned} \tag{B8}$$

The operator L_I is that part of L_+ due to the interactions among particles. Substitution of (B7) into (B8) gives the form (2.22),

$$\mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}')=\left[-a_{ij}k_i\frac{\partial}{\partial k_j}\delta_{\alpha\beta}+M_{\alpha\beta}(\mathbf{k};a)\right]\delta(\mathbf{k}-\mathbf{k}')\ , \tag{B9}$$

with $M_{\alpha\beta}(\mathbf{k};a)$ defined by

$$M_{\alpha\beta}(\mathbf{k};a)=\Lambda_{\alpha\sigma}(\mathbf{k};a)g^{-1}_{\sigma\beta}(\mathbf{k};a)\ , \tag{B10}$$

$$\Lambda_{\alpha\beta}(\mathbf{k};a)\equiv-(2\pi)^3V\langle X_\alpha(\mathbf{k})\tilde{z}^*_\beta(-\mathbf{k})\rangle\ , \tag{B11}$$

and $X_\alpha(\mathbf{k})$ is the phase function defined by Eq. (B8). Use has been made of the fact that the ensemble for uniform shear flow is translationally invariant at constant $\{\mathbf{p}'_n\}$, so all matrix elements are diagonal in $\mathbf{k},\mathbf{k}'$. Substitution of (B9)–(B11) into (B6) leads to

$$F_{\alpha\beta}(\mathbf{k},\mathbf{k}')=F_{\alpha\beta}(\mathbf{k};a)\delta(\mathbf{k}-\mathbf{k}') ,$$

$$F_{\alpha\beta}(\mathbf{k};a)=\Lambda_{\alpha\beta}(\mathbf{k},a)+\Lambda^*_{\beta\alpha}(\mathbf{k},a)-a_{ij}k_i\frac{\partial}{\partial k_j}g_{\alpha\beta}(\mathbf{k};a) . \tag{B12}$$

This is the generalized fluctuation-dissipation relation for the nonequilibrium stationary state of uniform shear flow. In the following we consider $\Lambda_{\alpha\beta}$ and $g_{\alpha\beta}$ as the fundamental quantities to be calculated. The nonzero elements of $F_{\alpha\beta}$ are determined from these by (B12). Any approximations introduced in calculating $\Lambda_{\alpha\beta}$ or $g_{\alpha\beta}$, therefore, will not violate (B12).

There are some important exact results that follow from the fact that $T_+(n,n')z_1(\mathbf{k})=0$. Since it is apparent from (A17) that $F_{\alpha\beta}$ is a Hermitian matrix, it follows from (A16) that

$$F_{\alpha 1}(\mathbf{k},\mathbf{k}')=0=F_{1\alpha}(\mathbf{k},\mathbf{k}') . \tag{B13}$$

In the same way, Eqs. (B8) and (B11) gives the result

$$\Lambda_{1\alpha}(\mathbf{k};a)=-ikg_{3\alpha}(\mathbf{k};a) . \tag{B14}$$

Similarly, $\Lambda_{\alpha 1}(k;a)$ can be obtained from (B13) and (B12),

$$\Lambda_{\alpha 1}(k;a)=-ikg^*_{3\alpha}(\mathbf{k};a)+a_{ij}k_i\frac{\partial}{\partial k_j}g_{\alpha 1}(\mathbf{k};a) . \tag{B15}$$

Both Eqs. (B14) and (B15) are exact. For the purposes here they are required only to first order in the shear rate, so (B15) can be written as

$$2\,\mathrm{Im}g_{3\alpha}(k;a)=-a_{ij}\hat{k}_i\hat{k}_j\frac{\partial}{\partial k}g^{(0)}_{11}(k)\delta_{\alpha 1} , \tag{B16}$$

where $g^{(0)}_{11}(k)=g_{11}(\mathbf{k};a=0)$. Below we introduce an approximation to calculate $g_{\alpha\beta}(\mathbf{k};a)$ by neglecting momentum correlations in the two- and three-particle reduced distribution functions. If applied to $g_{31}(\mathbf{k};a)$ this approximation implies $g_{31}\rightarrow 0$ in contradiction to the exact result (B16) (except for $\mathbf{k}$ orthogonal to $\hat{x}$ or $\hat{y}$). Instead we choose

$$g_{31}(\mathbf{k};a)\rightarrow -\tfrac{1}{2}a_{ij}\hat{k}_i\hat{k}_j\frac{\partial}{\partial k}g^{(0)}_{11}(k) , \tag{B17}$$

consistent with (B16), and apply the approximation below only to the other elements of the g matrix.

From the definition (2.17), $g_{\alpha\beta}(\mathbf{k};a)$ can be expressed in terms of the one- and two-particle reduced distribution functions for the stationary state,

$$g_{\alpha\beta}(\mathbf{k})=n\int d\mathbf{p}'_1 f(\mathbf{p}'_1)c_\beta(\mathbf{p}'_1)+n^2\int d\mathbf{p}'_1 d\mathbf{p}'_2 d\mathbf{q}_{12}c_\alpha(\mathbf{p}'_1)c_\beta(\mathbf{p}'_2)e^{i\mathbf{k}\cdot\mathbf{q}_{12}}[f^{(2)}(1,2)-f^{(1)}(1)f^{(1)}(2)] . \tag{B18}$$

To evaluate the second integral we make the approximation

$$f^{(2)}(1,2)\rightarrow f^{(1)}(1)f^{(1)}(2)G(\mathbf{q}_{12};a) , \tag{B19}$$

which implies negligible momentum correlations. As discussed above, this is not always valid for g_{31} and g_{13}, and should not be applied in these cases. Otherwise, we have no clear estimate of the importance of such correlations, but their neglect is not inconsistent with any of the above known exact properties. The spatial correlation function $G(\mathbf{q}_{12};a)$ is simply related to $g_{11}(\mathbf{k};a)$.

It remains to determine the stationary solution, $f^{(1)}(1)$. A closed equation follows from the first BBGKY hierarchy equation and (B19)

$$\begin{aligned}-a_{ij}p'_i\frac{\partial}{\partial p'_j}&f^{(1)}(\mathbf{p}')\\ &=n\int d\mathbf{p}_2 d\mathbf{q}_{12}\overline{T}_-(12)f^{(1)}(\mathbf{p}')\\ &\qquad\times f^{(1)}(\mathbf{p}'_2)G(\mathbf{q}_{12})+s(1) ,\end{aligned}$$

where $s(1)$ is a source due to the external forces. It is straightforward to solve this equation by the Chapman-Enskog method to first order in the shear rate a. The result is

$$f^{(1)}=f_0(p')[1-(12\nu^*y/\pi)a^*(\beta p'_x p'_y/2m)] . \tag{B21}$$

Here a^* and ν^* are the dimensionless shear rate and shear viscosity, defined by

$$\begin{aligned}\nu^*&\equiv\frac{5}{16n^*\chi}(1+\tfrac{4}{15}n^*X) ,\\ a^*&\equiv at_0,\quad t_0\equiv\sigma(\beta m\pi)^{1/2}/(4\pi n^*\chi) .\end{aligned} \tag{B22}$$

Also $n^*\equiv n\sigma^3$, $\chi\equiv G(\mathbf{q}_1-\mathbf{q}_2=\boldsymbol{\sigma})$, $y\equiv 2\pi n^*\chi/3$, and $f_0(p')$ is the Maxwell-Boltzmann distribution as a function of p'. This residual shear rate dependence in $\mathbf{p}'$ must also be accounted for to first order. The approximate matrix elements, $g_{\alpha\beta}(\mathbf{k};a)$, used in the model are then given by

$$\begin{aligned}&g_{11}(\mathbf{k};a)=m^2nS(\mathbf{k};a) ,\\ &g_{22}=3n/2\beta^2 ,\\ &g_{\alpha\beta}=(nm/\beta)[\delta_{\alpha\beta}-a^*(6\nu^*y/\pi)D_{\alpha\beta}],\quad \alpha,\beta=3-5 ,\end{aligned} \tag{B23}$$

with

$$\begin{aligned}D_{\alpha\beta}&\equiv e_x^{(\alpha)}e_y^{(\beta)}+e_y^{(\alpha)}e_x^{(\beta)} ,\\ S(\mathbf{k};a)&\equiv 1+n\int d\mathbf{q}_{12}e^{i\mathbf{k}\cdot\mathbf{q}_{12}}[G(\mathbf{q}_{12})-1] .\end{aligned} \tag{B24}$$

Also, $g_{31}=g^*_{13}$ is given by (B17); all other matrix elements are zero.

Next, consider $\Lambda_{\alpha\beta}(\mathbf{k};a)$. From (B14), (B15), and (B23) we find

$$\begin{aligned}\Lambda_{1\alpha}(\mathbf{k};a)&=-ikg_{31}(\mathbf{k};a)\delta_{\alpha 1} ,\\ \Lambda_{\alpha 1}(\mathbf{k};a)&=-\Lambda^*_{1\alpha}(\mathbf{k};a)-\delta_{\alpha 1}a_{ij}k_i\frac{\partial}{\partial k_j}g^{(0)}_{11}(k) .\end{aligned} \tag{B25}$$

The remaining matrix elements must be calculated directly from (B11). The result is similar to that of (B18) except that now the three-particle reduced distribution function appears as well. We introduce an approximation such as (B19) to evaluate such terms,

$$f^{(3)}(1,2,3)\to f^{(1)}(1)f^{(1)}(2)f^{(1)}(3)G(\mathbf{q}_{12},\mathbf{q}_{13};a) . \tag{B26}$$

Then, for $\alpha\neq 1$ and $\beta\neq 1$, the terms contributing to $\Lambda_{\alpha\beta}(k;a)$ up to first order in a are

$$\begin{aligned}\Lambda_{\alpha\beta}(\mathbf{k};a)=&\Gamma_{\alpha\sigma}g^{(0)}_{\sigma\beta}(\mathbf{k})-\frac{n}{m}\int d\mathbf{p}'_1 f^{(1)}(p'_1)c_\alpha(\mathbf{p}')i\mathbf{k}'\cdot\mathbf{p}'_1 c_\beta(\mathbf{p}'_1)\\ &-n^2X\int d\mathbf{p}'_1 d\mathbf{p}'_2 d\mathbf{q}_{12}c_\beta(\mathbf{p}'_1)f^{(1)}(p'_1)f^{(1)}(p'_2)T_+(12)[c_\alpha(\mathbf{p}'_1)+e^{-i\mathbf{k}\cdot\boldsymbol{\sigma}}c_\alpha(\mathbf{p}'_2)] ,\end{aligned} \tag{B27}$$

where $\Gamma_{\alpha\beta}$ is defined by

$$\Gamma_{\alpha\beta}\equiv e_x^{(\alpha)}e_y^{(\beta)}-e_i^{(\alpha)}k_x\frac{\partial e_i^{(\beta)}}{\partial k_y}, \quad \alpha,\beta=3-5 . \tag{B28}$$

The matrix elements, $M_{\alpha\beta}(\mathbf{k};a)$ are obtained by matrix multiplication of the above results for $\Lambda_{\alpha\beta}(\mathbf{k};a)$ and $g_{\alpha\beta}(\mathbf{k};a)$ retaining terms to order a. The results are most conveniently given in dimensionless form, with the definitions

$$\begin{aligned}&k^*\equiv k\sigma, \quad \overline{M}_{\alpha\beta}\equiv t_0(\bar{h}_\alpha^{-1}M_{\alpha\beta}\bar{h}_\beta) \ \text{(no sum on } \alpha \text{ or } \beta) ,\\ &\bar{h}_\alpha\equiv(m,\beta^{-1}\sqrt{m/\beta},\sqrt{m/\beta},\sqrt{m/\beta}) .\end{aligned} \tag{B29}$$

Then $\overline{M}_{\alpha\beta}$ can be written as

$$\overline{M}_{\alpha\beta}(k^*,a^*)=M^{(0)}_{\alpha\beta}(k^*)+a^*M^{(1)}_{\alpha\beta}(k^*) . \tag{B30}$$

The nonzero matrix elements of $M^{(0)}_{\alpha\beta}(k^*)$ are found to be

$$\begin{aligned}&M^{(0)}_{13}=-ik^*\sqrt{\pi}/6y, \quad M^{(0)}_{31}=M^{(0)}_{13}/S_0(k^*) ,\\ &M^{(0)}_{22}=\tfrac{2}{3}[1-j_0(k^*)] ,\\ &M^{(0)}_{23}=M^{(0)}_{13}[1+3yj_1(k^*)/k^*] ,\\ &M^{(0)}_{32}=\tfrac{2}{3}M^{(0)}_{23} ,\\ &M^{(0)}_{33}=(\tfrac{2}{3})[1-3j_0(k^*)+6j_1(k^*)/k^*] ,\\ &M^{(0)}_{44}=M^{(0)}_{55}=(\tfrac{2}{3})[1-3j_1(k^*)/k^*] ,\end{aligned} \tag{B31}$$

where $j_n(k^*)$ is the nth-order spherical Bessel function and $S_0(k^*)\equiv S(k^*,a^*=0)$. Similarly, the nonzero matrix elements of $M^{(1)}_{\alpha\beta}(k^*)$ are

$$\begin{aligned}&M^{(1)}_{21}=M_0(k_xk_y/k^2), \quad M^{(1)}_{22}=M_1(k_xk_y/k^2) ,\\ &M^{(1)}_{2\beta}=i(M_2+\delta_{\beta 3}M_3)(\Gamma_{3\beta}+\Gamma_{\beta 3}) ,\\ &M^{(1)}_{\alpha 1}=\delta_{\alpha 3}i\left[k^*\left[\frac{\partial}{\partial a^*}\ln S(k^*;a^*)\right]_{a^*=0}-M^{(0)}_{33}\frac{6y}{\sqrt{\pi}}\frac{\partial}{\partial k^*}\ln S_0(k^*)\Gamma_{33}\right]\\ &\qquad +iM_4(\Gamma_{\alpha 3}+\Gamma_{3\alpha}), \quad \alpha=3-5 ,\\ &M^{(1)}_{\alpha 2}=i(\delta_{\alpha 3}M_5+M_6)(\Gamma_{\alpha 3}+\Gamma_{3\alpha}), \quad \alpha=3-5 ,\\ &M^{(1)}_{\alpha\beta}=\Gamma_{\alpha\beta}+[M_7+M_8(\tfrac{1}{2}\delta_{\alpha\beta}+\delta_{\alpha 3}+\delta_{\beta 3})+\delta_{\alpha 3}\delta_{\beta 3}M_9](\Gamma_{\alpha\beta}+\Gamma_{\beta\alpha}), \quad \alpha,\beta=3-5 .\end{aligned} \tag{B32}$$

The functions $M_n(k^*)$ are

$$\begin{aligned}&M_0=M^{(0)}_{23}\frac{i6y}{\sqrt{\pi}}\frac{\partial}{\partial k^*}\ln S_0(k^*) , \qquad M_1=-3y\left[1+\frac{20\nu^*}{3\pi}\right]j_2(k^*) ,\\ &M_2=\frac{12y}{\sqrt{\pi}}\left[1+\frac{\nu^*}{2}\right]\frac{1}{k^*}j_2(k^*)-\frac{\nu^*}{\sqrt{\pi}}k^* , \qquad M_3=-\frac{6y}{\sqrt{\pi}}\left[(1+\tfrac{1}{2}\nu^*)j_3(k^*)+\tfrac{1}{2}M^{(0)}_{21}\frac{\partial S(k^*)}{\partial k^*}\right] ,\\ &M_4=\nu^*k^*/S(k^*), \quad M_5=-\frac{y}{\sqrt{\pi}}(1+4\nu^*)j_3(k^*) , \qquad M_6=\frac{y}{\sqrt{\pi}}(1+4\nu^*)\frac{1}{k^*}j_2(k^*)+\tfrac{4}{3}\nu^*k^* ,\\ &M_7=-\frac{2y}{3}\left[\left[1+\frac{2\nu^*}{\pi}\right]\left[1-\frac{15}{k^{*2}}j_2(k^*)\right]+\frac{10\nu^*}{\pi}\left[1-\frac{3}{k^*}j_1(k^*)\right]\right]+\nu^*M^{(0)}_{44} ,\\ &M_8=-3y\left[1+\frac{2\nu^*_k}{\pi}\right]\frac{1}{k^*}j_3(k^*) , \qquad M_9=2M_8-\nu^*_k\left[M^{(0)}_{44}-M^{(0)}_{33}+\frac{12y}{\pi}j_2(k^*)\right]-iM^{(0)}_{31}\frac{6y}{\sqrt{\pi}}\frac{\partial S_0(k^*)}{\partial k^*} ,\\ &M_{10}=-3y\left[1+\frac{2\nu^*_k}{\pi}\right]\left[j_2(k^*)-\frac{7}{k^*}j_3(k^*)\right] .\end{aligned} \tag{B33}$$

The structure factor $S_0(k)$ and the pair correlation function at contact are evaluated using the Percus-Yevick integral equation. The only remaining unknown is $\partial S(k^*,a^*)/\partial a^*$ at $a^*=0$. For the special case of $\mathbf{k}$ along the y axis (i.e., along the direction of the macroscopic velocity gradient) these terms do not contribute and the only nonvanishing elements of $M^{(1)}_{\alpha\beta}$ are $M^{(1)}_{24}$, $M^{(1)}_{41}$, $M^{(1)}_{42}$, $M^{(1)}_{34}$, and $M^{(1)}_{43}$.

Finally, the matrix elements of the force amplitude are given by Eq. (B12), for α and $\beta\neq 1$.

$$F_{\alpha\beta}(k;a)=\Lambda_{\alpha\beta}(k;a)+\Lambda^*_{\beta\alpha}(k;a) \ . \tag{B34}$$

Also, $F_{1\alpha}=0=F_{\alpha 1}$ as indicated in Eq. (B5).

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