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Stability Analysis of a Dense Hard-Sphere Fluid Subjected to Large Shear—Shear-Induced Ordering

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The stability at finite wave numbers of a hard-sphere fluid subjected to a large shear is examined by use of hard-sphere kinetic theory. For a fixed density, for molecular-scale wave numbers, and for a critical shear rate the fluid is found to become unstable with respect to density waves in the direction of the velocity gradient. The critical shear rates obtained are close to those found by Erpenbeck in his nonequilibrium molecular-dynamics simulations of shear-induced ordering.

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In recent years nonequilibrium molecular-dynamics (NEMD) techniques have been used to study the properties of simple fluids under steady shear.[1-7] Typically, the shear rates in these computer simulations are orders of magnitude larger than those obtainable in real laboratory situations. Nevertheless, there has been considerable interest in these computer experiments since the dependence of the shear viscosity η on the shear rate $\dot{\epsilon}$ is very similar to that obtained experimentally for supercooled molecular liquids under realistic shear.[8] Early computer simulations measured $\eta(\dot{\epsilon})$ and the nonequilibrium contributions to the normal stresses.

In a recent Letter, Erpenbeck[6] used NEMD to show that for a large enough shear rate a three-dimensional hard-sphere fluid underwent a phase transition. In particular, Erpenbeck found that if the fluid flow is planar Couette flow and is given by $u_\alpha = x\dot{\epsilon}\delta_{\alpha y}$ ($\alpha = x,y,z$), then for a fixed density of hard spheres there is a critical shear rate where a phase transition to a two-dimensional ordered state occurred. Snapshots of the particles indicated that in the ordered state the positions of the particles in the x and z directions were arranged on what appears to be a two-dimensional triangular lattice. We note that the phase transition occurs when the variation in the flow field is comparable to a molecular diameter. Finally, we stress that the density of particles is less than the equilibrium freezing density for hard-sphere fluids.

Physically, one expects Erpenbeck's transition to be almost continuous since a tendency for fluid layering is present for any $\dot{\epsilon}$. Motivated by this, we have performed a linear stability analysis of a hard-sphere fluid undergoing planar Couette flow. For a fixed density we find that at a critical shear rate $\dot{\epsilon}_c$, the fluid becomes unstable with respect to a density wave in the x direction. Our value for $\dot{\epsilon}_c$ is quite close to the value obtained by Erpenbeck[6] for the critical shear rate where the fluid freezes into a two-dimensional ordered solid. We tentatively conclude that they are related.

Our analysis is complicated compared to usual stability analysis[9] for several reasons. First, the shear rates are not small. As a consequence of this one cannot simply keep terms linear in the shear rate. Second, the critical wave-number regime is not at small wave numbers but at intermediate wave numbers near where the equilibrium static structure factor has its maximum. Physically this is obvious since the ordering takes place on a molecular scale. Because of this one cannot use the hydrodynamic equations but instead one must use either generalized[10] (to finite wave number) hydrodynamic equations or kinetic theory. In our analysis we used hard-sphere kinetic theory. However, in order to make our calculations accessible to a larger audience we will relate our kinetic-theory analysis to a generalized nonequilibrium hydrodynamic-equations approach. The kinetic theory will be used to obtain, approximately, the generalized thermodynamic and transport coefficients to be used in these equations. We believe that this is the first time that a generalized nonequilibrium hydrodynamics has been derived and used for a stability analysis far from equilibrium.

The basic idea used here is that already in thermal equilibrium, density fluctuations are very slowly decaying near wave numbers where the static structure factor $S(k)$, with k the wave number, has its first maximum. These slowly decaying intermediate-length-scale density fluctuations have been discussed in detail elsewhere.[11-13] Here we examine the possibility that because of the shear rate this already small relaxation rate vanishes. Our starting equation is the revised Enskog equation (RET) for hard-sphere fluids.[14] At the densities Erpenbeck considers, this kinetic equation is known[11] to do an excellent job of describing equilibrium density fluctuations near $k = k_0$, where $S(k)$ has its maximum. Here we assume that the RET also correctly describes density fluctuations near k_0 in the presence of shear. We note that by this approximation we neglect mode-coupling effects. The RET is given by

$$[\partial_t + \mathbf{v}_1 \cdot \partial/\partial \mathbf{r}_1] f(1,t) = \int d2\, \overline{T}_-(12) g(\mathbf{r}_1, \mathbf{r}_2 t) f(1,t) f(2,t), \tag{1}$$

where $f(1,t)$ $(1 = \mathbf{r}_1, \mathbf{v}_1)$ is the one-particle distribution function at position $\mathbf{r}_1$ and velocity $\mathbf{v}_1$ at time t. $g(\mathbf{r}_1, \mathbf{r}_2, t)$ is the pair-distribution function for an inhomogeneous equilibrium fluid at number density $n(\mathbf{r}_1, t) = \int d^3 v_1 f(1,t)$. $\overline{T}_-(12)$ in Eq. (1) is a hard-sphere collision operator that is given elsewhere[14] and which takes into account the difference in position between two colliding particles. Finally, we remark that it can be easily shown that the RET in equilibrium reduces to the density functional theories[15] used in modern treatments of equilibrium freezing.

To perform the stability analysis we first linearize Eq. (1) about the average state of the fluid described macroscopically by a uniform number density n_0, a flow velocity given by $u_\alpha(x) = x\dot{\epsilon}\delta_{\alpha y}$, and a uniform and constant temperature T (we neglect viscous heating). The microscopic state of the fluid is described by the steady-state (ss) distribution function f_{ss}. When we write $f(1,t) = f_{ss}(1) + \delta f(1,t)$, the fluctuation $\delta f(1,t)$ in the distribution function satisfies the equation

$$[\partial_t + \mathbf{v}_1 \cdot \partial/\partial \mathbf{r}_1] \delta f(1,t) = g(\sigma) \int d2\, \overline{T}_-(12)(1 + P_{12}) f_{ss}(2) \delta f(1,t) + \int d2\, d^3 r_3\, \overline{T}_-(12) f_{ss}(1) f_{ss}(2) H(\mathbf{r}_1 \mathbf{r}_2 | \mathbf{r}_3) \delta n(\mathbf{r}_3, t), \tag{2}$$

where $g(\sigma)$ is the radial distribution function at contact, with σ the hard sphere diameter and

$$H(\mathbf{r}_1 \mathbf{r}_2 | \mathbf{r}_3) = [\delta g(\mathbf{r}_1, \mathbf{r}_2, t)/\delta n(\mathbf{r}_3, t)]_{\mathrm{eq}} \tag{3}$$

is the functional derivative of $g(\mathbf{r}_1, \mathbf{r}_2, t)$ evaluated in a uniform or equilibrium fluid of density n_0. H in Eq. (3) can be expressed in terms of equililbrium two- and three-point correlation functions. f_{ss} in Eq. (2) satisfies a steady-state nonlinear Enskog equation. Equation (2) is the starting equation in our linear stability analysis.

Rather than examining the stability properties of Eq. (2) directly, it is sufficient to examine velocity moments of $\delta f(1,t)$. In particular, the density fluctuations,

$$\delta n(\mathbf{r}_1, t) = \int d^3 v_1\, \delta f(1,t), \tag{4}$$

will play an essential role in our analysis. Also important are velocity fluctuations δu_α, given by

$$n(\mathbf{r}_1, t)[u_\alpha(x_1) + \delta u_\alpha(\mathbf{r}_1, t)] - n_0 u_\alpha(x_1) = \int d^3 v_1\, v_{1\alpha} \delta f(1,t). \tag{5}$$

Elsewhere[13] one of us showed that in thermal equilibrium, density fluctuations in a dense hard-sphere fluid at wave numbers near k_0 were well described by what is effectively a moment solution of Eq. (2) retaining only the four moments of δf given by Eqs. (4) and (5).[16] Our detailed calculations suggest that this is also true in the nonequilibrium steady state considered here. With this approximation, closed hydrodynamiclike equations for δn and δu_α can be easily derived. By a Fourier-Laplace (with variable z) transform of these equations we have obtained

$$z\delta n(\mathbf{k}, z) - \dot{\epsilon} k_y\, \partial \delta n(\mathbf{k}, z)/\partial k_x + n_0 i k\, \delta u_l(\mathbf{k}, z) = \delta n(\mathbf{k}, 0), \tag{6a}$$

and

$$z\delta u_\alpha(\mathbf{k},z) - \dot\epsilon k_y \frac{\partial}{\partial k_x}\delta u_\alpha(\mathbf{k},z) + \delta_{\alpha y}\dot\epsilon\,\delta u_x(\mathbf{k},z)$$
$$= \delta u_\alpha(\mathbf{k},0) - \frac{ik_\alpha \delta n(\mathbf{k},z)}{\beta m n_0 S(k)} - \Gamma_{\alpha n}(\mathbf{k},\epsilon)\delta n(\mathbf{k},z) - \Gamma_{\alpha l}(\mathbf{k},\dot\epsilon)\delta u_l(\mathbf{k},z) - \sum_{i=1}^{2}\Gamma_{\alpha t_i}(\mathbf{k},\dot\epsilon)\delta u_{t_i}(\mathbf{k},z). \tag{6b}$$

Here we have introduced a set of three orthonormal unit vectors, $(\hat{\mathbf{k}},\hat{\mathbf{k}}_\perp^1,\hat{\mathbf{k}}_\perp^2)$, with $\hat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$ a unit vector in the direction of $\mathbf{k}$; $\delta u_l(\mathbf{k},z)=\hat{\mathbf{k}}_\alpha \delta u_\alpha(\mathbf{k},z)$ is the longitudinal velocity and $\delta u_{t_i}(\mathbf{k},z)=\mathbf{k}_{\perp\alpha}^i\delta u_\alpha(\mathbf{k},z)$ are the transverse velocities. Here summation convention has been used. The k-derivative terms in Eqs. (6) arise from the convective terms ($\sim \mathbf{u}\cdot\nabla$) in the hydrodynamic equations in real space. In these equations $\beta=(k_\mathrm{B}T)^{-1}$, with k_B Boltzmann's constant, m is the mass of the particles, $S(k)$ is the equilibrium static structure factor, and $\delta n(\mathbf{k},0)$ and $\delta u_\alpha(\mathbf{k},0)$ are initial-condition terms. The Γ's in Eq. (6b) are in the literature[11-13] for a hard-sphere fluid in equilibrium and their explicit form for the nonequilibrium steady state considered here will be given elsewhere. They are obtained from the moment solution of Eq. (2). Here we restrict ourselves to terms of $O(\dot\epsilon^2)$ and we will discuss the validity of the approximation below. To determine approximate expressions for the Γ's we first have solved the ss Enskog equation for f_ss to $O(\dot\epsilon^2)$. It is then straightforward to establish that the Γ's depend on equilibrium two- and three-point correlation functions, the dimensionless wave number $k\sigma$, the reduced density $n_0\sigma^3$, and the reduced shear rate $\dot\epsilon t_0$, with t_0 the Boltzmann mean free time between collisions in a hard-sphere fluid.[11] Here we note that the leading terms in an $\dot\epsilon$ expansion of the Γ's follow from general considerations. That is, $\Gamma_{\alpha n}\sim O(\dot\epsilon)$, $\hat{k}_\alpha\Gamma_{\alpha l}=\Gamma_{ll}\sim O(\dot\epsilon^0)$, $\hat{k}_{\perp\alpha}^i\Gamma_{\alpha t_i}=\Gamma_{t_it_i}\sim O(\dot\epsilon^0)$, $\Gamma_{t_il}\sim O(\dot\epsilon)\sim\Gamma_{lt_i}$, $\Gamma_{t_it_j}(i\neq j)\sim O(\dot\epsilon)$. These estimates will be used below.

Before solving Eqs. (6) we make some further simplifications. We are interested in examining the decay of density waves and we separately consider $\delta n(\mathbf{k}=k_x\hat{\mathbf{x}},z)=\delta n_x(k_x,z)$, $\delta n_y(k_y,z)$, and $\delta n_z(k_z,z)$. We first note that it is physically obvious, and easily confirmed by calculation, that δn_z depends only weakly on $\dot\epsilon$ and we therefore concentrate on δn_x and δn_y. Examining Eqs. (6) we see that there is a fundamental difference between δn_x and δn_y. The equations for δn_y contain a differential operator in k space, while the equations for δn_x do not. As a consequence of this it is not too hard to show that $\delta n_y(k_y,t)$ always decays faster than $\delta n_x(k_x,t)$. Therefore we consider here only $\delta n_x(k_x,z)$. This is an important simplification since for $\mathbf{k}=(k_x,0,0)$ Eqs. (6) reduce to algebraic equations. For these values of $\mathbf{k}$ and the estimates for Γ given above, Eqs. (6) can be easily solved to $O(\dot\epsilon^2)$. For long times, or $z\to 0$, and $|k_x|\sim k_0$, $\delta n_x(k_x,z)$ satisfies the equation

$$[z+\omega(k_x,\dot\epsilon)]\delta n_x(k_x,z)=\delta n(k_x,0), \tag{7a}$$

with

$$\omega(k_x,\epsilon)=\frac{k_x^2 A(k_x,\dot\epsilon)}{\beta m S(|k_x|)\Gamma_{ll}(k_x,\dot\epsilon)B(k_x,\dot\epsilon)}, \tag{7b}$$

where

$$A(k_x,\dot\epsilon)=1-\frac{i\beta m n_0 S(|k_x|)}{|k_x|}\Gamma_{ln}(k_x,\dot\epsilon)+\frac{i\beta m n_0 S(|k_x|)}{|k_x|}\sum_{i=1}^{2}\frac{\Gamma_{lt_i}(k_x,\epsilon)\Gamma_{t_in}(k_x,\dot\epsilon)}{\Gamma_{t_it_i}(k_x,\dot\epsilon)}+O(\dot\epsilon^4), \tag{7c}$$

and

$$B(k_x,\dot\epsilon)=1-\sum_{i=1}^{2}\frac{\Gamma_{lt_i}(k_x,\dot\epsilon)[\dot\epsilon\hat{k}_{\perp y}^i\hat{k}_x+\Gamma_{t_il}(k_x,\dot\epsilon)]}{\Gamma_{ll}(k_x,\dot\epsilon)\Gamma_{t_it_i}(k_x,\dot\epsilon)}+O(\dot\epsilon^4). \tag{7d}$$

Here we have set $\delta u_\alpha(k_x,0)=0$ for convenience. Equations (7) represent our final results. From symmetry arguments it follows that the terms in Eqs. (7c) and 7(d) (except for the 1) are of $O(\dot\epsilon^2)$ and that they are correct to $O(\dot\epsilon^4)$. For $\dot\epsilon\to O$, Eqs. (7a) and (7b) give the slowly decaying intermediate–length-scale ($|k_x|\sim k_0$) equilibrium density mode discussed in detail elsewhere.[11-13] We also note that $\delta n_x(k_x,z)$ becomes critical if $\omega(k_x,\dot\epsilon)$, or $A(k_x,\dot\epsilon)$ vanishes for any k_x and $\dot\epsilon$ at a fixed density.

Using our explicit results for the Γ's we find that this happens in a region where we believe that our theory is qualitatively accurate. In calculating the Γ's we have used the Verlet-Weiss–corrected Percus-Yevick representation[17] for $S(k)$ and the Kirkwood superposition approximation for the three-point equilibrium correlation functions that appear. The contributions from the terms involving three-point correlation functions turn out to be small and so we do not believe that the use of the Kirkwood superposition approximation is an important approximation in our theory. For $n\sigma^3 \simeq 0.88$, we find that $A(k_x, \dot{\epsilon})$ vanishes at $|k_x|\sigma \simeq 6.7$, and a critical shear rate $(\dot{\epsilon} t_0)_c = \dot{\epsilon}_c^* = 0.33$. Here t_0 is the Boltzmann mean free time between collisions for hard-sphere particles. At this density Erpenbeck[6] observes a phase transition at $\dot{\epsilon}^* \simeq 0.4$. For $n\sigma^3 \simeq 0.704$, we find that $A(k_x, \dot{\epsilon})$ vanishes at $|k_x|\sigma \simeq 6.4$ and a critical shear rate $(\dot{\epsilon} t_0)_c = \dot{\epsilon}_c^* = 0.61$. Erpenbeck[6] observes a transition at $\dot{\epsilon}^* \simeq 0.8$, although the transition region is very broad at this density. We note that both our critical shear rates and the scale where density fluctuations become unstable are quite reasonable.

We conclude by discussing our results and the approximations we have used.

(1) In our calculations we have neglected viscous heating effects. Furthermore, in Erpenbeck's simulations viscous heating is prevented by a velocity-rescaling technique. The effects of this velocity rescaling are not included in our starting kinetic equation. We remark that viscous-heating terms first appear in the problem in the unperturbed distribution function as contributions of $O(\dot{\epsilon}^2)$. However, for symmetry reasons we can show that these terms do not contribute to the quantity A in Eq. (7b). If the same were to be true for the effects of velocity rescaling then we could conclude that with regard to this point our calculation of A is correct to $O(\dot{\epsilon}^2)$.

(2) In our calculation of $A(k_x, \dot{\epsilon})$ we have retained only terms of $O(\dot{\epsilon}^2)$ and neglected those of $O(\dot{\epsilon}^4)$. We remark that to $O(\dot{\epsilon}^2)$ by far the largest contribution comes from the local equilibrium contribution to f_{ss}. Furthermore, we note that if we replace f_{ss} by its local equilibrium contribution then there are no contributions to $A(k_x, \dot{\epsilon})$ from Γ_{ln} [which is the largest contribution of $O(\dot{\epsilon}^2)$] of $O(\dot{\epsilon}^4)$. This suggests that the $O(\dot{\epsilon}^4)$ terms are all small. Preliminary calculations also suggest this. Technically the terms of $O(\dot{\epsilon}^4)$ always involve very complicated angular factors that integrate to small numerical coefficients.

(3) We note that the instability discussed above for $\delta n_x(k_x, t)$ is independent of the convective terms in the generalized hydrodynamic equation since they vanish for $\mathbf{k} = (k_x, 0, 0)$. In our calculations we can identify two effects that are due to the shear and which cause the instability. First, the normal stresses in the fluid are modified to $O(\dot{\epsilon}^2)$ and they contribute to terms of this order in $A(k_x, \dot{\epsilon})$. Second, the density and shear-rate dependence of the generalized (to finite k) transport coefficients also leads to terms of $O(\dot{\epsilon}^2)$ in $A(k_x, \dot{\epsilon})$. In our calculations the latter terms are much larger than the former terms.

Finally, we point out that we have not attempted to describe the ordered state in this Letter.

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Note added.—After this paper was submitted we received a preprint by D. J. Evans and G. P. Morriss. These authors have used NEMD to show that a two-dimensional soft-sphere fluid under large shear is extremely sensitive to the type of thermostatting used. For what they consider an unbiased thermostat they find that the fluid becomes turbulent at a critical shear rate. Our results cannot distinguish between the development of an ordered state or a turbulent state since we perform only a linear stability analysis.

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