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Possible Instability for Shear-Induced Order-Disorder Transition

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A simple fluid in uniform isothermal shear flow is studied for conditions used in recent nonequilibrium computer simulations. The short-time dynamics for the local conserved densities is found to be unstable at large shear rates for wave vectors near the peak of the structure factor. The critical shear rates obtained are similar to those for an order-disorder transition observed in the computer simulations.

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Nonequilibrium computer simulations of a simple fluid in uniform shear flow have uncovered a number of unexpected properties for states far from equilibrium. One of the most interesting and least understood is a transition from the disordered fluid phase to an ordered fluid phase, as reported recently by Erpenbeck[1] for hard spheres and by others for continuous potentials.[2] The ordered phase consists of layers (analogous to smectic liquid crystals) normal to the velocity gradient. Furthermore, particles within a layer are concentrated in tubes along the direction of flow, and these tubes are hexagonally packed relative to adjacent layers. The control parameter is the shear rate, a, and the transition is signaled by a dramatic decrease of the shear viscosity at the critical shear rate. The system considered by Erpenbeck is a hard-sphere fluid at two "liquid" densities, $n^* = 0.88$ and 0.704, where $n^* = n\sigma^3$ and σ is the hard-sphere diameter. The range of shear rates considered was $0 < a^* < 1.6$, where $a^* = at_0$ and t_0 is the Boltzmann mean free time. Such shear rates are many orders of magnitude larger than typical laboratory values, but analogous shear-induced ordered phases are observed in complex colloidal suspensions.[3]

One possible explanation for the transition in simple fluids is a hydrodynamic instability. A perturbation analysis[4] of the hydrodynamic equations for shear flow indicates stability up to $a^* \sim 0.05$; this is consistent with the computer simulations, where the transition occurs for shear rates an order of magnitude larger. However, Kirkpatrick and Nieuwoudt[5] have recently reported an instability in a kinetic theory model for the domain of large wave vectors and shear rates for which the order-disorder transition is observed. Their values of the critical shear rate and its density dependence are in qualitative agreement with those for the order-disorder transition. The purpose here is to report the results of a stability analysis that is similar in spirit, but with a somewhat more complete analysis of the hydrodynamic modes. The description is obtained from the short-time dynamics of the stationary-state time correlation functions, with the Lees-Edwards boundary conditions and thermostat forces used in the computer simulations. The imposed shear is found to induce qualitative changes in the hydrodynamics. For example, at large wave vectors there is a range of shear rates for which the heat mode and one of the shear modes become a propagating pair. At larger shear rates this pair is unstable. The minimum shear rate for instability occurs at wave vectors near the peak of the static structure factor and directed along the velocity gradient. The minimum values for this instability also occur at shear rates similar to those for the order-disorder transition.

The hydrodynamic equations for a simple fluid are the usual macroscopic local conservation laws for mass, energy, and momentum, supplemented by constitutive equations for the irreversible energy and momentum fluxes. For wavelengths long compared to the mean free path the latter are given by the Navier-Stokes forms.

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The usual form also assumes that the wavelengths are large compared to the atomic correlation length, so that the susceptibilities can be approximated by corresponding thermodynamic derivatives. However, at high densities the mean free path is smaller than the correlation length and it is possible to study phenomena with wavelengths comparable to the correlation length. In this case the effects of the correlation length on the susceptibilities and transport coefficients must be accounted for. Such generalized hydrodynamic equations have been discussed recently by several people to describe the dynamics of equilibrium fluctuations,[6-9] and the calculation here is an extension to the stationary state for shear flow. The most interesting consequence of this generalization for our purposes is a softening of the heat mode by several orders of magnitude near the peak of the structure factor. The existence of this soft mode, although always stable in equilibrium, provides a potential source for an instability under external constraints. The calculations here and in Ref. 5 identify a mechanism whereby the imposed shear further softens the heat mode until it becomes unstable.

In the computer simulation, the Lees-Edwards boundary conditions induce viscous heating as a consequence of the average shear flow.[10,11] To maintain a steady state additional nonconservative forces are introduced to extract heat at the same rate as it is produced by the shear. It is possible to show[12] that the corresponding macroscopic local conservation laws for mass, energy, and momentum density (denoted as ρ, u, and $\mathbf{p}$, respectively) admit an exact solution with constant density and internal energy density, and a flow velocity, $\mathbf{v}_0$,

$$v_{0i}(\mathbf{r}) = a_{ij} r_j, \quad a_{ij} \equiv a\delta_{ix}\delta_{jy}. \tag{1}$$

The shear-rate tensor, a_{ij}, has been defined so that the flow is along the x direction with a constant gradient, a, along the y direction.

To study the stability of uniform shear flow, we look for possible growth of small deviations in ρ, u, or $\mathbf{p}$ from their steady-state values. A Fourier representation for the deviations of the hydrodynamic variables from the uniform shear state is denoted by $\{y_1(\mathbf{k},t)\}$. For a wide class of initial conditions, the dynamics is determined by the steady-state time correlation functions for the local conserved densities,

$$\begin{aligned} y_{1\alpha}(\mathbf{k},t) &= \textstyle\sum_{k'} G_{\alpha\beta}(\mathbf{k},t;\mathbf{k}',0) y_{1\beta}(\mathbf{k}',0), \\ G_{\alpha\beta}(\mathbf{k},t;\mathbf{k}'0) &\equiv \textstyle\sum_{k''} C_{\alpha\sigma}(\mathbf{k},t;\mathbf{k}'',0) C_{\sigma\beta}^{-1}(\mathbf{k}'',0;\mathbf{k}',0), \\ C_{\alpha\beta}(\mathbf{k},t;\mathbf{k}',0) &\equiv \langle \psi_\alpha(\mathbf{k},t)[\psi_\beta(k',0) - \langle \psi_\beta(\mathbf{k}',0)\rangle]\rangle. \end{aligned} \tag{2}$$

The angular brackets denote an average over the stationary-state ensemble for uniform shear flow. Equation (2) expresses the relationship of linear stability for that flow to the decay or growth of fluctuations. The specific variables, ψ_α, chosen here are the Fourier transformed mass, energy, and momentum density measured in the rest frame (i.e., as functions of the relative momentum, $p'_{ni} \equiv p_{ni} - m a_{ij} q_{nj}$). Extending standard techniques for equilibrium correlation functions to the case of interest here, we obtain a formally exact set of linear equations for $\{y_1\}$,

$$\frac{\partial y_{1\alpha}(\mathbf{k},t)}{\partial t} + \textstyle\sum_{k'} \mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}';t) y_{1\beta}(\mathbf{k}',t) = 0. \tag{3}$$

Our primary approximation is to restrict attention to the short-time structure of this equation by evaluating $\mathcal{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}';t)$ at $t = 0^+$. A special feature of hard-sphere fluids is that the short-time dynamics includes finite momentum transfer, which typically requires a finite time to develop for fluids with continuous potentials. Consequently, short-time approximations for hard spheres are often applicable even in the hydrodynamic domain. No restrictions on the density, wave vector, or shear rate are imposed in this limit. Our main justification for its use here is that it is known to be good approximation in equilibrium,[8] and we expect that this qualitative feature should extend to the stationary state.

Considerable simplification occurs in this limit, and Eq. (3) has a local form

$$\left(\frac{\partial}{\partial t} - a_{ij} k_i \frac{\partial}{\partial k_j}\right) y_{1\alpha}(\mathbf{k},t) + M_{\alpha\beta}(\mathbf{k},a) Y_{1\beta}(\mathbf{k},t) = 0. \tag{4}$$

We look for an instability associated with $\mathbf{k}$ along the direction of the velocity gradient ($k_x = k_z = 0$). In this case the "hydrodynamic" modes are determined from the eigenvalue problem

$$M_{\alpha\beta}(\mathbf{k},a) \psi_\beta^{(i)}(\mathbf{k},a) = \lambda^{(i)}(\mathbf{k},a) \psi_\alpha^{(i)}(\mathbf{k},a). \tag{5}$$

The eigenvalues, $\lambda^{(i)}(\mathbf{k},a)$, are either real or complex conjugate pairs. An instability is indicated when any of the real parts of $\lambda^{(i)}(\mathbf{k},a)$ vanish. The matrix elements $M_{\alpha\beta}(\mathbf{k},a)$ can be reduced to functionals of the one-, two-, and three-particle reduced distribution functions for the stationary state. Three-particle correlations are then expressed in terms of pair correlations by use of a nonequilibrium stationarity constraint. The range of wave vectors relevant for the computer simulation includes $k\sigma \gg 1$. Consequently, expansion in powers of k is not appropriate. On the other hand, the order-disorder transition is observed at a reduced shear rate $a^* \sim 0.4$ (at the highest density), and expansion in a^* might be marginally acceptable. We have assumed this is the case, at least for determining qualitative features such as the instability, and $M_{\alpha\beta}(\mathbf{k},a)$ has been evaluated as a function of $\mathbf{k}$ to first order in the shear rate. The five eigenvalues and eigenvectors can then be determined explicitly.

At zero shear rate and small wave vectors, the eigenvalues represent two sound modes, two shear modes, and a heat diffusion mode. As the wave vector is increased, the heat-mode eigenvalue softens (decreases) by more

than three orders of magnitude, relative to its small wave vector form, with a minimum for k near the peak of the structure factor. Figure 1 shows the effect of shear rate on this mode softening for $n^* = 0.88$. For the two densities considered by Erpenbeck, $n^* = 0.88$ and 0.704, the critical shear rate occurs at $a_c^* = 0.63$ and 0.85, respectively. Figure 2 shows the dependence of the critical shear rate on density; also shown are the results of Erpenbeck, $a_c^* = 0.4$ and 0.8. Since the values of the critical shear rates found here and their density dependence are similar to those for the order-disorder transition, it is reasonable to speculate that the latter arises from this or a related type of hydrodynamic instability.

Some further comments for clarification and context are as follows:

(1) The instability described here is associated with the heat mode, which is already soft at large wave vectors for zero shear rate as a result of effects of atomic structure on the hydrodynamics. The additional softening at large shear rates is due to a coupling of longitudinal-momentum variations to the transverse-momentum variations in the direction of flow. The wave-vector dependence of the transport coefficients is important; consequently, the instability is the result of an interesting interplay of atomic structure and macroscopic hydrodynamics far from equilibrium.

(2) In addition to the stability analysis, it is straightforward to calculate the eigenvectors. The eigenvectors for the modes are then a known linear combination of the conserved densities whose dynamics could be simulated to study more directly the predicted instability. For example, the unstable mode can be identified as due almost entirely to density deviations from the uniform shear state which couple into initial density, temperature, and velocity fields. A density inhomogeneity $\delta\rho(\mathbf{r}) \sim \cos(ky)$ prepared initially will have a dominant contribution

$$\delta\rho(\mathbf{r},t)/\delta\rho(\mathbf{r}) \sim e^{-\lambda(k,a)t} \tag{6}$$

for k near the peak of the structure factor and shear rates near the instability. In Eq. (6), $\lambda(k,a)$ is the eigenvalue which vanishes at a_c^*. Typically the behavior (6) should occur for t larger than a few collision times. Simulation of this density response would provide a good check of the predicted instability.

(3) The most serious approximation used here (and in Ref. 5) is the assumption that the shear rate, a^*, may be treated as an expansion parameter. For the state conditions considered, $a^* \sim 1$ near the instability and this assumption is questionable. It has been argued[5] that the angle averages in $M_{\alpha\beta}(\mathbf{k},a)$ may diminish higher-order powers of a^*. We plan to check the validity of such expansions by a numerical calculation of the dominant matrix elements.

(4) Kirkpatrick and Nieuwoudt's analysis is similar to that presented here and likewise associates the order-disorder transition with a hydrodynamic instability. However, they include contributions to $M_{\alpha\beta}(k,a)$ of order a^2, whereas we have included terms only to first order in a. The dominant term in each calculation is associated with an additional normal stress along the direction of the gradient of the shear flow. Here, this term couples longitudinal and transverse velocity components and is of order $\Delta P_{yy} \sim ak^2 p_{1x}$. Kirkpatrick and Nieuwoudt attribute their instability to a coupling of the longitudinal velocity to density variations of order $\Delta P_{yy} \sim a^2 k \rho_1$. These two nonequilibrium effects are present in both models, but which dominates depends on the quantitative estimates of their coefficients in each model. In both Ref. 5 and here static correlations are ultimately approximated by equilibrium correlations. However, the approximation is introduced at the beginning of the former calculation while it is used at the end of the present calculation. This seems to be the primary source of difference in the two models since postpone-

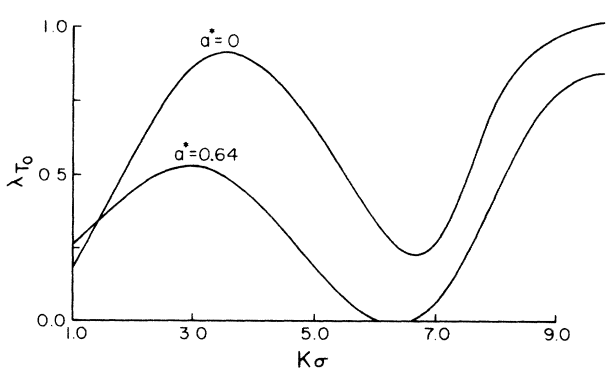

FIG. 1. Heat-mode softening vs $k\sigma$ for $n^* = 0.88$ at shear rates $a^* = 0.0$ and 0.64; the latter case indicates an instability near $k\sigma \sim 6$.

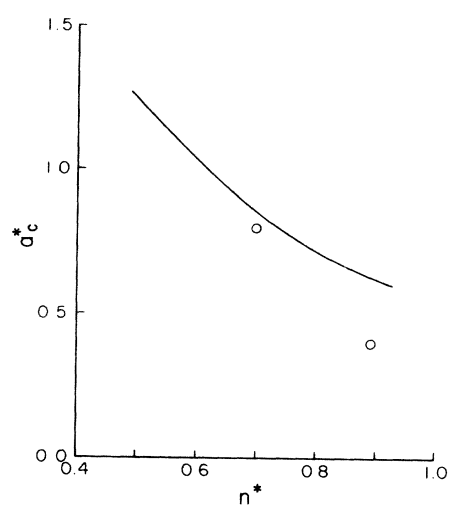

FIG. 2. Minimum critical shear rate vs density (solid line). Also shown are Erpenbeck's values for the order-disorder transition (circles).

ment of the approximation allows us to avoid the Kirkwood superposition approximation used in Ref. 5. Both studies should therefore be understood as primarily directed at identifying the qualitative features of a shear-induced instability. Quantitative accuracy may well depend on a better understanding of the relative importance of nonequilibrium momentum correlations.

(5) The linear hydrodynamic modes calculated here can be used to determine the effects of nonlinear mode coupling. It is possible that the resulting renormalized modes could be modified significantly near the instability. No attempt has been made here to determine such effects.

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[1]J. J. Erpenbeck, Phys. Rev. Lett. **52**, 1333 (1984).

[2]See, for example, L. V. Woodcock, Phys. Rev. Lett. **54**, 1513 (1985); S. Hess, J. Phys. (Paris), Colloq. **46**, C3-191 (1985).

[3]B. J. Ackerson and N. A. Clark, Phys. Rev. A **30**, 906 (1984), and Physica (Amsterdam) **118A**, 221 (1983).

[4]J. Lutsko and J. W. Dufty, Phys. Rev. A **32**, 3040 (1985); J. W. Dufty and J. Lutsko, in *Recent Developments in Nonequilibrium Statistical Mechanics,* edited by J. Casas-Vazquez (Springer-Verlag, Berlin, 1986).

[5]T. R. Kirkpatrick and J. C. Nieuwoudt, Phys. Rev. Lett. **56**, 885 (1986).

[6]I. de Schepper and E. G. D. Cohen, Phys. Rev. A **22**, 287 (1980).

[7]W. E. Alley and B. J. Alder, Phys. Rev. A **27**, 3158 (1983).

[8]T. R. Kirkpatrick, Phys. Rev. A **32**, 3130 (1985).

[9]J. Keizer and M. Medina-Noyola, Physica (Amsterdam) **115A**, 301 (1982).

[10]A. Lees and S. F. Edwards, J. Phys. C **5**, 1921 (1972).

[11]J. W. Dufty, A. Santos, J. J. Brey, and R. Rodriguez, Phys. Rev. A **33**, 459 (1986).

[12]J. W. Dufty, J. J. Brey, and A. Santos, in "Molecular Dynamics Simulation of Statistical Mechanical Systems," International School of Physics "Enrico Fermi," Course 97, edited by G. Ciccotti and W. G. Hoover (North-Holland, Amsterdam, to be published).