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Glass transition and self-consistent mode-coupling theory

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The implications of a self-consistent mode-coupling theory of dense fluids for the liquid-glass transition are considered. First, we show that when higher-order corrections are ignored from our model, there is a dynamic transition of the hard-sphere fluid at an intermediate density to an ideal glassy phase. This is in agreement with earlier theoretical works. Next, we demonstrate that in the present model there is a cutoff mechanism that rounds off the sharp transition. We compute the transport coefficients for the hard-sphere fluid, which show good agreement with computer-simulation results at supercooled densities. The viscosity follows a power-law increase for the intermediate densities with an exponent close to 2. For very high densities the sharp transition is cut off and the transport coefficient increases at a slower rate. We calculate how the density autocorrelation function in a Lennard-Jones fluid decays in time. This is done for different densities along an isotherm. Our results agree much better with the slow relaxation observed in molecular-dynamics simulations than earlier theories.

I. INTRODUCTION

Mode-coupling theories have been applied to supercooled metastable states of a fluid in an attempt to develop a theory for an ideal glass transition. The basic mechanism that increases the viscosity was first identified by Leutheusser[1] from kinetic theory of dense fluids. A similar model was proposed by Bengtzelius, Götze, and Sjölander.[2] Nonlinear fluctuating hydrodynamics was also applied[3] to understand the model. In these theories attention was focused on mode-coupling effects that arise from density fluctuations only, in view of the fact that they become dominant at such high densities. This involves a nonlinear feedback to the transport coefficients from the dynamic correlation of density fluctuations in the fluid. It was shown that at sufficiently high density, this feedback mechanism results in an ideal glass transition where the density autocorrelation function no longer decays to zero in the long-time limit and the viscosity of the fluid diverges. This is essentially a dynamic transition and the static properties are not affected by it. However, the exact location of the transition[4] for a specific system is dependent on the structure of the fluid.

In Ref. 5 a more complete treatment of the nonlinear fluctuating hydrodynamics for compressible fluid was done by Das and Mazenko. The analysis involved the development of a Martin-Siggia-Rose (MSR)-type field theory for the dynamics of the fluctuating variables, constrained by the nonlinear relation $\mathbf{g}=\rho\mathbf{v}$, where $\mathbf{g}$ is the momentum density, ρ is the mass density, and $\mathbf{v}$ is the velocity field. The main new result obtained was the prediction of a rounded version of the transition due to a mechanism that keeps the system ergodic for all values of the density. Subsequently, a similar model was also reported by Götze and Sjoren[6] from a more microscopic approach.

Computer simulation[7] of simple fluids is a useful tool for understanding their static as well as their dynamic properties. Ullo and Yip[8] have done molecular-dynamics simulations on a system of particles interacting through a truncated and purely repulsive Lennard-Jones (LF) potential. They reported a substantial slowing down of relaxation in the fluid at very high densities. But it was also found that, in comparison to their results, the simple feedback mechanism predicts a much stronger effect and this results in an ideal glass transition at an intermediate density. In the present work we apply the model proposed in Ref. 5 to more specific systems by including a proper equilibrium structure for the fluid and compare the theoretical results with the computer simulation results at supercooled densities.

The effect of including a realistic structure factor on the dynamic feedback mechanism was also considered in an earlier work.[9] The present model has several improvements. In Ref. 5 we approximated the static structure factor with a Lorentzian form and thus in computing the mode-coupling effects we could only include contributions from length scales up to the first peak of the structure factor for the fluid. Here we are not restricted to any such functional form and thus the mode-coupling integrals can be computed up to length scales that are more typical for such calculations.[10] Since we are interested in the relaxation properties at finite wavelengths, here we take into account wave-vector-dependent transport coefficients for the linear theory as well. To compute the dynamic nonlinearity in the present model, we consider the proper free-energy functional that was also used in density-functional[11] theories as well as in earlier works[10] on mode-coupling theory for dense fluids. We are now able to make more direct contact with models obtained from the microscopic approach. The present work thus demonstrates the role of the cutoff mechanism in explaining the results of computer simulations of fluids at metastable densities.

Since the basic model was described in considerable details in Ref. 5, we will avoid any formal description of the model here. In comparing our results with the specific models we take into account both hard-sphere fluids and one-component Lennard-Jones fluid. We use the Percus-Yevick (PY) solution[12] for the static structure factor of the hard-sphere system. In case of the Lennard-Jones fluid we use perturbative methods standard in literature[13] to compute the thermodynamic properties. Our main results are as follows.

(i) When we ignore all nonhydrodynamic corrections (terms higher order in wave number) then we make direct contact with other models obtained from a more microscopic approach. We show that a hard-sphere fluid undergoes a sharp transition to an ideal glassy phase at the density $n_0\sigma^3=0.99$, where σ is the diameter of the hard sphere. This is in agreement with the result of Bengtzelius *et al.*[4] In the glassy phase the density autocorrelation function for the fluid freezes to a nonzero value in the long-time limit.

(ii) Next we consider the complete model and compute the longitudinal and shear viscosities for a hard-sphere fluid, taking into account the mode-coupling contributions. This is done for different densities ranging from intermediate to very high values. It is found that for intermediate densities the viscosity follows a power-law divergence form with an exponent $\alpha=2.0$. But for very high densities, the sharp transition is cutoff and the viscosity now increases at a slower rate. In Ref. 14 a similar behavior was also reported for a large number of laboratory systems, where the exponent of the power law varies from 1.6 to 2.3 for different systems. We compute the diffusion coefficient from the shear viscosity using the Stokes-Einstein relation. Our result is close to that obtained by Angell[5] and Woodcock from simulation of a hard-sphere system at metastable densities.

(iii) For a Lennard-Jones system we show how the density correlation function decays in time and this is compared with the corresponding data from the molecular-dynamics simulation of Ullo and Yip. This is done for several densities along the isotherm $T^*=0.60$. For the sake of comparison, we also present here the solution from the model without the cutoff mechanism. The latter clearly indicates a too-enhanced mode-coupling effect while the results from the complete model with the cutoff mechanism shows a much better agreement.

In the present work we have compared our solutions with results from computer simulation of simple systems whose static properties can be computed easily and this is a necessary input in our calculation of the dynamics. The results we have reported in this paper suggest that our model provides a good explanation for the increase of viscosity in systems termed as fragile[16] glasses, indicating a power-law behavior over the intermediate density regime. However, the slowing down indicated here for computer liquids is still quite far from what is observed in more complex systems terms as "strong" glasses. The characteristic time scales for such systems fall up to 14 orders of magnitude following a strong Arrhenius-type behavior. Transport in these systems is an activated process and any such mechanism is absent in the present theory. We believe it is necessary to go beyond mode-coupling theories to provide an explanation for such a dramatic slowing down of the transport processes with supercooling.

The paper is organized as follows: In Sec. II we describe briefly the model studied, and give the one-loop expressions for the mode-coupling integrals. In Sec. III we demonstrate how our model makes contact with other works that predict a sharp glass transition. In Sec. IV we solve the complete model. Here we present the results obtained for a hard-sphere system as well as a LJ system and compare them with molecular-dynamics simulations. We end the paper with a discussion of the results in Sec. V.

II. DESCRIPTION OF THE MODEL

A. Generalized hydrodynamic equations

We start with the set of hydrodynamic variables consisting of the mass density ρ, and momentum density $\mathbf{g}$, and the flow velocity $\mathbf{v}$. For a compressible fluid they are constrained by the nonlinear relation

$$\mathbf{g}=\rho\mathbf{v} \ . \tag{1}$$

We neglect the temperature fluctuations to keep analysis simple. The average density is denoted by ρ_0 and it is related to the number density n_0 as $\rho_0=mn_0$ where m, is the mass of the particles in the fluid. Next we write down the equations of motion for the hydrodynamic variables. They can be deduced using the well-known Zwangig-Mory[17] formalism and are valid for small and finite wavelengths. The equation for ρ is given by

$$\frac{\partial\rho}{\partial t}=-\nabla\cdot\mathbf{g} \tag{2}$$

and that for g is the generalized nonlinear Navier-Stokes equation

$$\frac{\partial g_i}{\partial t}=-\rho\nabla_i\frac{\delta F_u}{\delta\rho}-\sum_j\nabla_j(g_iv_j)-\sum_j\int dx' L_{ij}(x-x')\frac{\delta F}{\delta\rho(x')}+\Theta_i \ , \tag{3}$$

where L_{ij} is the bare transport matrix and Θ_i is the thermal noise.

$F_u[\rho(x)]$ is the potential-energy part of the effective Hamiltonian F governing the equilibrium behavior of the hydrodynamic variables. Thus we have

$$F=F_K+F_u \ , \tag{4}$$

where the kinetic-energy term F_K is given by[18]

$$F_K=\tfrac{1}{2}\int d^3x\, g^2(x)/\rho(x) \ . \tag{5}$$

For the potential part F_u of the free-energy functional we choose the expansion of an inhomogeneous equilibrium liquid. This is the usual form chosen in the density-functional theories and is given by

$$F_u[\rho(x)]=F_0[\rho]+F_{\mathrm{int}}[\rho] \ , \tag{6}$$

with F_0 being the ideal gas entropy term

$$\beta m F_0[\rho]=\int dx\, \rho(x)\{\ln[\rho(x)/\rho_0]-1\} \tag{7}$$

and $F_{\rm int}$ is the interaction term. To lowest order this can be written up to a constant as

$$\beta m F_{\rm int}[\rho]=-\frac{1}{2m}\int d^3x\, d^3x' c^{(2)}(x-x')\delta\rho(x)\delta\rho(x') , \tag{8}$$

with

$$\delta\rho(x,t)=\rho(x,t)-\rho_0$$

and $\beta=1/k_BT$. $c(x)$ is the equilibrium two-particle correlation function. This form of the free-energy functional was also used earlier in computing the mode-coupling contribution[10] for a dense fluid. It gives the appropriate wave-vector-dependent vertex functions for the nonlinear terms in Eq. (3). We are ignoring here direct correlation functions beyond the two-point level. However, due to the ideal gas term, the free-energy functional is not strictly Gaussian. Since our main interest here is in the dynamic properties of the fluid, to avoid technical complications we assume that higher-order terms do not affect the statics in any serious way. The equilibrium structure factor for the fluid can be expressed in terms of $c(x)$. Thus in the Fourier space we have

$$S(k)=[1-n_0c(k)]^{-1} .$$

Using Eqs. (4) and (6), the hydrodynamic equation for **g** can be written as

$$\begin{aligned}\frac{\partial g_i(x,t)}{\partial t}=&-\frac{\partial}{\partial x_i}\int d^3x' U(x,x')\delta\rho(x',t)-\sum_j\frac{\partial}{\partial x_j}[g_i(x,t)v_j(x,t)]\\&-\int d^3x_1 d^3x_2 V^{(i)}(x,x_1,x_2)\delta\rho(x_1,t)\delta\rho(x_2,t)-\sum_j\int dx' L_{ij}(x-x')v_j(x',t)+\Theta_i(x,t) ,\end{aligned} \tag{9}$$

where

$$U(x,x')=\frac{1}{\beta m^{(i)}}[\delta(x-x')-n_0c(x-x')] \tag{10}$$

and the quadratic vertex $V^{(i)}$ is given by

$$V^{(i)}(x,x_1,x_2)=\frac{1}{\beta m^2}\left[\delta(x-x_2)\frac{\partial}{\partial x_i}c(x-x_1)+\delta(x-x_1)\frac{\partial}{\partial x_i}c(x-x_2)\right] . \tag{11}$$

For an isotropic fluid the bare transport matrix $L_{ij}(\mathbf{x})$ or its Fourier transform

$$L_{ij}(q)=\int dx\, e^{i\mathbf{q}\cdot\mathbf{x}}L_{ij}(x) \tag{12}$$

can be expressed in terms of two independent transport coefficients given by

$$L_{ij}(q)=q_iq_j\Gamma^0(q)+(q^2\delta_{ij}-q_iq_j)\eta^0(q) . \tag{13}$$

In the small-wave-number limit, $\Gamma^0(q)$ and $\eta^0(q)$ are the bare longitudinal and shear viscosities, respectively. Since we will be applying these equations for finite wavelengths here, more generalized expressions for these quantities are necessary. These results are more dependent on the specific models used and since most of our results are related to hard-sphere systems, we will use the Enskog-type expressions[19] for this purpose which describe the short-time behavior for the fluid quite well. These were obtained from more microscopic models and have the following forms:

$$q^2\Gamma^0(q)=\frac{2\rho_0}{3t_E}[1-j_0(q\sigma)+2j_2(q\sigma)] \tag{14}$$

and

$$q^2\eta^0(q)=\frac{2\rho_0}{3t_E}[1-j_0(q\sigma)-j_2(q\sigma)] . \tag{15}$$

The noise Θ_i is Gaussian and satisfies

$$\langle\Theta_i(\mathbf{x},t)\Theta_j(\mathbf{x}',t')\rangle=2k_BTL_{ij}(\mathbf{x})\delta(\mathbf{x}-\mathbf{x}')\delta(t-t') . \tag{16}$$

Equations (2) and (9) together with the nonlinear constraint (1) defines our model. In order to investigate what effects the nonlinearities in these equations will have on the transport properties of the fluid, we need to develop a formalism convenient for renormalizing the linear theory. For this purpose we construct a field theory of the Martin-Siggia-Rose[20] (MSR) type, which is standard in the literature for studying the statistical properties of a classical nonlinear system. This formulation of a self-consistent renormalized theory was described in considerable detail in Ref. 5. Since the present work is intended for describing the quantitative effects produced in a real system, we will state here the final results with the proper mode-coupling integrals necessary for numerical calculation. The advantage of using MSR field theory here is that we can obtain the renormalized expressions for the various quantities in a self-consistent manner in terms of the full Green's functions. This is very useful in demonstrating the feedback mechanism that results in slow relaxation at high densities.

B. Renormalization

The main quantity of interest here is the density autocorrelation function whose Fourier transform is defined as

$$G_{\rho\rho}(q,t)=\int d(\mathbf{x}-\mathbf{x}')e^{i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')}\langle\delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x}',0)\rangle , \tag{17}$$

where the angular brackets refer to the average over the stationary states. We will use the following normalized form for the Fourier transform of $G_{\rho\rho}$ given by

$$\psi(q,t)=\frac{G_{\rho\rho}(q,t)}{\chi_{\rho\rho}(q)} . \tag{18}$$

$\chi_{\rho\rho}$ stands for the equal-time value of the density correlation function. For an isotropic fluid the correlation function among the **g** fields can be expressed in terms of the longitudinal and transverse components. Thus,

$$G_{g_i g_j}(q)=\hat{q}_i\hat{q}_j G^L_{gg}(q)+(\delta_{ij}-\hat{q}_i\hat{q}_j)G^T_{gg}(q) . \tag{19}$$

Note that the longitudinal part G^L_{gg} can be obtained in terms of the time derivatives of $G_{\rho\rho}$ using the continuity equation. We also define the following normalized transverse-current correlation function,

$$\phi(q,t)=\frac{G^T(q,t)}{\chi^T_{gg}(q)} , \tag{20}$$

where χ^T_{gg} stands for the equal-time transverse-current correlation functions.

It was shown in Ref. 5 that the renormalized theory for the nonlinear fluctuating hydrodynamics of compressible fluids obtains the following form for the Laplace transform of the density correlation function:

$$\psi(q,z)=\frac{z+iq^2\Gamma^R(q,z)}{z^2-q^2c^2(q)+iq^2\Gamma^R(q,z)[z+iq^2\gamma(q,z)]} . \tag{21}$$

Here

$$c^2(q)=[\beta m S(q)]^{-1}$$

and $\Gamma^R(q,z)$ is the renormalized longitudinal viscosity. The quantity $\gamma(q,z)$ arises from the nonlinear constraint (1) and hence reflects the effect of coupling between the density fluctuations and current fluctuations in a compressible fluid. Similarly, the Laplace transform for the transverse-current fluctuation is given by

$$\phi(q,z)=\frac{1}{z+iq^2\eta^R(q,z)} , \tag{22}$$

where $\eta^R(q,z)$ is the renormalized shear viscosity. In the formulation of the MSR-type field theory the renormalized quantities on the right-hand side (rhs) of Eqs. (21) and (22) are expressed in terms of the correlation functions on the other side and thus constitute a self-consistent theory. We will use one-loop expressions for renormalizations of the various quantities. Since at very high densities the mode-coupling contribution is dominated by density fluctuations, we ignore the effects coming from the convective nonlinearities. We include only the terms involving density correlation and its coupling to current fluctuation, the latter being important for a compressible fluid. The renormalized transport coefficients can be expressed in terms of the effective mode-coupling functions, denoted by the superscript MC, as

$$q^2\Gamma^R(q,z)=q^2\Gamma^0(q)+\int_0^\infty dt\, e^{izt}\Gamma^{\rm MC}(q,t) \tag{23}$$

and

$$q^2\eta^R(q,z)=q^2\eta^0(q)+\int_0^\infty dt\, e^{izt}\eta^{\rm MC}(q,t) . \tag{24}$$

As explained above, the one-loop expressions for these mode-coupling functions are

$$\begin{aligned}q^2\Gamma^{\rm MC}(q,t)=\lambda_0\int d\mathbf{k}\frac{1}{(2\pi)^3}\{(\hat{\mathbf{q}}\cdot\mathbf{k})c(k)\\+[\hat{\mathbf{q}}\cdot(\mathbf{q}-\mathbf{k})]c(|\mathbf{q}-\mathbf{k}|)\}^2\\\times G_{\rho\rho}(\mathbf{q}-\mathbf{k},t)G_{\rho\rho}(\mathbf{k},t)\end{aligned} \tag{25}$$

and

$$\begin{aligned}q^2\eta^{\rm MC}(q,t)=\lambda_0 d\mathbf{k}\frac{1}{(2\pi)^3}[c(k)-c(|\mathbf{q}-\mathbf{k}|)]^2\\\times k^2(1-u^2)G_{\rho\rho}(\mathbf{q}-\mathbf{k},t)G_{\rho\rho}(\mathbf{k},t) ,\end{aligned} \tag{26}$$

where $\lambda_0=(2\beta m^4\rho_0)^{-1}$ and $u=\hat{\mathbf{q}}\cdot\hat{\mathbf{k}}$ while $\hat{\mathbf{q}}$ is the unit vector along the direction of **q**. The quantity $\gamma(q,z)$ in the rhs of Eq. (21) is given by

$$\gamma(q,z)=\int_0^\infty dt\, e^{izt}\gamma(q,t) \tag{27}$$

and $\gamma(q,t)$ can be written as the sum of two parts,

$$\gamma=\gamma_L+\gamma_T , \tag{28}$$

where

$$\begin{aligned}\gamma_L(q,t)=\frac{\beta c^2(q)}{2\rho_0^3}\int d\mathbf{k}\frac{1}{(2\pi)^3}\dot{G}_{\rho\rho}(\mathbf{q}-\mathbf{k},t)\dot{G}_{\rho\rho}(\mathbf{k},t)\\\times\frac{u}{k}\left[\frac{u}{k}+\frac{u_1}{|\mathbf{q}-\mathbf{k}|}\right]\end{aligned} \tag{29}$$

and

$$\gamma_T=\frac{\beta c^2(q)}{2\rho_0^3}\int d\mathbf{k}\frac{1}{(2\pi)^3}G_{\rho\rho}(\mathbf{q}-\mathbf{k},t)G^T_{gg}(\mathbf{k},t)(1-u^2) . \tag{30}$$

$\dot{G}$ refers to the time derivative of the function $G_{\rho\rho}(q,t)$ and $u_1=\hat{\mathbf{q}}\cdot\hat{\mathbf{d}}_{qk}$, where $\hat{\mathbf{d}}_{qk}$ is the unit vector in the direction of $(\mathbf{q}-\mathbf{k})$. We will demonstrate here that this quantity γ provides a mechanism that cuts off the sharp transition of the fluid to an ideal glassy phase. This is a consequence of the nonlinear constraint (1) for a compressible fluid. Formal expression was obtained in Ref. 5 for the quantity γ using nonperturbative analysis. However, for explicit calculations we use the one-loop results stated above. These were obtained from a small q,ω analysis. A more complete theory should involve a better approximation for γ obtained from a finite q and ω analysis. In the absence of a more general expression for this quantity we will use here the above form for finite wavelength also. The final results are thus not independent of the upper cutoff Λ in the wave-vector integration. It is not clear at this point what proper expression for the quantity γ may result in removing this dependence. However, in order to maintain consistency, we have kept the upper cutoff fixed throughout at a constant value which is typically used in computing mode-coupling integrals.

Before solving the complete model, we will first ignore the quantity γ and obtain the model which has an instability at high density. In Sec. III we demonstrate how the nonlinear feedback mechanism, involving only the density fluctuations, gives rise to a freezing in the nonergodic phase which was identified as an ideal glassy state.

III. SHARP TRANSITION TO NONERGODIC PHASE: DYNAMIC INSTABILITY IN THE SIMPLE MODEL

If we ignore the quantity γ in Eq. (21), we obtain

$$\psi(q,z)=\frac{z+iq^2\Gamma^R(q,z)}{z^2-q^2c^2(q)+iq^2z\Gamma^R(q,z)} . \tag{31}$$

This model has an instability that was first shown by Bengtzelius *et al.* In order to see this, let us assume that in the ideal glassy phase the density correlation function $\psi(q,t)$ develops a nondecaying part $f(q)$ in the long-time limit, i.e.,

$$\psi(q,t)=f(q)+\psi_v(q,t) , \tag{32}$$

where $\psi_v(q,t)$ goes to zero as t becomes large. Now using Eq. (32) in Eqs. (23) and (31) and then taking the long-time limit, we obtain the following nonlinear integral equation for $f(q)$:

$$\frac{f(q)}{1-f(q)}=\frac{1}{q^2c^2(q)}\Gamma^{\mathrm{MC}}(q,t\to\infty) , \tag{33}$$

where Γ^{MC} is given by Eq. (25). Equation (33) can be solved numerically by iteration obtaining a final set of $f(q)$. In order to compute the vertex functions in the mode-coupling integrals, we use the Percus-Yevick structure factor for a hard-sphere fluid. The fluid is considered to have undergone a transition when all the $f(q)$'s simultaneously converge on a nonzero set of values. We obtained such a transition at the critical density $\rho_c\sigma^3=0.99$. This is in agreement with the result quoted in Ref. 2. Figure 1 shows how final $f(q)$ varies with the wave number at this density. The exact location of the transition point thus depends on the static structure for the fluid. We choose the upper cutoff for the wave vector $k\sigma$ in the mode-coupling integrals such that $\Lambda\sigma=25$. It is found that contributions coming from wave vector above this value do not affect the transition point much.

Next we write down the equation (31) in the time space as a nonlinear integro-differential equation for the density correlation function,

$$\ddot{\psi}(q,t)+q^2\Gamma^0(q)\dot{\psi}(q,t)+q^2c^2(q)\psi(q,t)+\int_0^t d\tau\,\Gamma^{\mathrm{MC}}(q,t-\tau)\dot{\psi}(q,\tau)=0 . \tag{34}$$

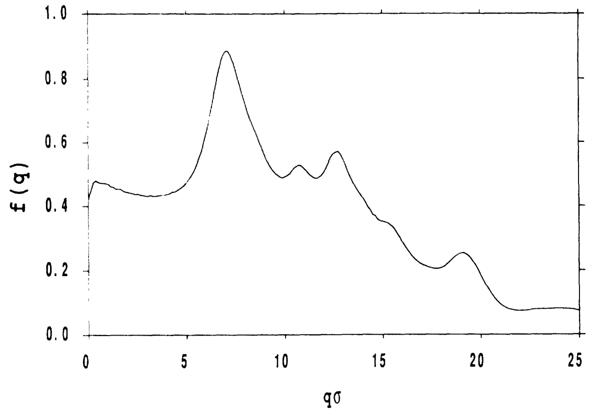

FIG. 1. The long-time limit of the density correlation function $f(q)$, computed from the simple model at the density $n^*=0.99$.

This equation can be solved numerically to obtain $\psi(q,t)$ as a function of q and t. In Sec. IV we will use this result to compare the model described above with computer-simulation results and also with a more consistent treatment of the mode-coupling theory which is described in the next section.

IV. CUTOFF MECHANISM FOR THE COMPRESSIBLE FLUID

Now we return to the full expression (21) for the density correlation functon retaining the nonhydrodynamic quantity γ. We show that when γ is solved self-consistently with ψ, the instability described in Sec. III is absent even at very high densities. Thus the density autocorrelation function does not freeze in the long-time limit and always decays to zero, maintaining ergodicity. However, due to mode-coupling effects the system still slows down with the increase of density. This was demonstrated in Ref. 1 for a simple but unphysical model where all structural effects were ignored by considering a static structure factor for the liquid that is independent of wave number. In the present work we evaluate the mode-coupling effects taking into account the proper wave-vector dependence in the theory and investigate how this affects the relaxation of the density correlation for different values of the wave number.

First, we write down Eqs. (21) and (22) in the time space as a coupled set of nonlinear integro-differential equations:

$$\ddot{\psi}(q,t)+q^2\Gamma^0(q)\dot{\psi}(q,t)+q^2c^2(q)\psi(q,t)+\int_0^t d\tau\,\Gamma^{\mathrm{MC}}(q,t-\tau)\dot{\psi}(q,\tau)$$
$$+q^2\int_0^2 d\tau\,\gamma(q,t-\tau)\left[q^2\Gamma^0(q)\psi(q,\tau)+\int_0^\tau d\tau_1\Gamma^{\mathrm{MC}}(q,\tau-\tau_1)\psi(q,\tau_1)\right]=0 \tag{35}$$

and

$$\dot{\phi}(q,t)+q^2\eta^0(q)\phi(q,t)+\int_0^t \eta^{\mathrm{MC}}(q,t-\tau)\phi(q,\tau)d\tau=0 \; . \tag{36}$$

We solve these equations numerically to obtain $\psi(q,t)$ and $\phi(q,t)$ as functions of q and t. As the renormalized shear viscosity in Eq. (22) gets large due to mode-coupling contributions, the transverse-current correlation function decays very fast and hence in the actual calculation we ignore γ_T compared to the longitudinal part γ_L to ease the computation. We have used in these calculations the same value for the upper cutoff of the wave-vector integration, i.e., $k\sigma=25$, as in Sec. III. The whole wave-vector range is divided by a grid of size 200. As the density gets very high, we need to go to smaller time steps in order to solve the above integro-differential equations numerically and thus the process gets more time consuming. We describe our main results for a hard sphere and Lennard-Jones system, respectively, as follows.

A. Hard-sphere fluid

We use the PY solution for the static structure factor of the hard-sphere fluid. In Fig. 2 we show how the density autocorrelation function at the first diffraction peak decays in time for several different densities. The behavior is qualitatively very similar to what is observed by Ullo and Yip in their computer simulations with a one-component Lennard-Jones fluid. It was shown in Sec. III that in the simple mode-coupling model where γ is ignored, $\psi(q,t)$ does not decay to zero above $n^*=0.99$. Thus the quantity γ results in avoiding the complete freezing of the fluid into a nonergodic phase. However, with the increase of density the mode-coupling effects gets bigger and the quantity γ also gets smaller and as a result there is some remnant of the sharp transition. To indicate the slowing down of relaxation due to mode-coupling effects, we show in Fig. 3 how the quantity $\gamma(0,0)$ decreases as the density of the fluid is increased. Although this quantity falls with the increase of density, it does not go to zero rapidly enough, which could make the case for a strong glassy behavior. Next we compute the shear and longitudinal viscosities including the mode-coupling contributions. In Fig. 4 the behavior of

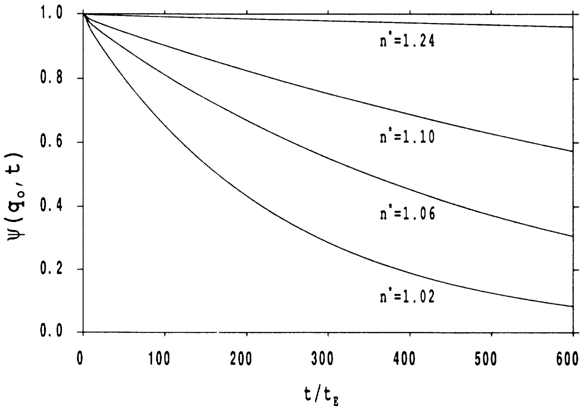

FIG. 2. The normalized density correlation function $\psi(q_0,t)$, where q_0 is at the first peak in the structure factor, for different densities of a hard-sphere fluid.

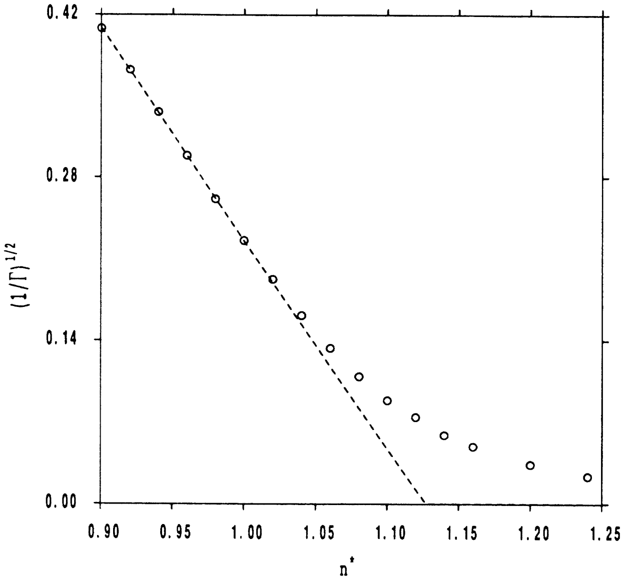

FIG. 3. Square root of the inverse of the normalized longitudinal viscosity $\bar{\Gamma}$ vs density. The dashed line shows the power-law fit for intermediate densities.

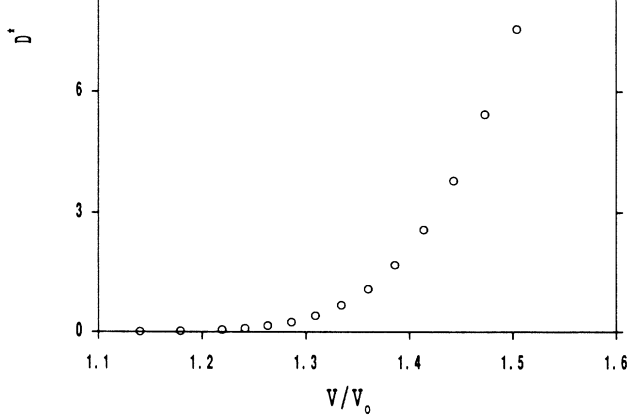

FIG. 4. The diffusion coefficient as a function of the reduced volume of the hard-sphere fluid, V_0 being the close-packed volume.

the longitudinal viscosity with density is shown. We have expressed the result in terms of the bare longitudinal viscosity defined as $\bar{\Gamma}=\Gamma(0,0)/\Gamma^0(0)$. In the low-density regime the viscosity follows a power-law divergence with an exponent of $\alpha=2.0$. But for higher densities it increases at a slower rate, cutting off the sharp transition. This qualitatively agrees with the behavior observed in a large number of systems, as was reported by Taborek *et al.* This involves a power-law increase of the viscosity over an intermediate temperature regime, higher than is normally associated with glass transition. The exponent lies in the range of 1.5 to 2.3. From the data for shear viscosity, we compute the self-diffusion coefficient (D) for a hard-sphere fluid using the Stokes-Einstein relation. In accordance with Woodcock and Angell, we define the dimensionless quantity D^* as

$$D^*=\frac{10^3}{\sigma}\left[\frac{m}{k_BT}\right]^{1/2}D\ . \tag{37}$$

In Fig. 5 this is plotted as a function of the reduced volume V/V_0 where V_0 is the close-packed volume. It shows power-law behavior similar to the longitudinal viscosity with the same exponent α. The actual values for the diffusion coefficient obtained in the present theory are close to that reported by Angell and Woodcock from their molecular-dynamics simulation with hard-sphere fluids at metastable densities. It was already pointed out elsewhere[3] that this computer-simulation data can also be fitted very well to a power-law form with an exponent 1.86. For relatively lower densities, the present form of the self-consistent mode-coupling approximation seems to give a somewhat smaller value for the diffusion coefficient than the simulation results. Next, in Fig. 6, we show how the transverse-current correlation function $\phi(q,t)$ behaves with time for $q\sigma=1.0$ at $\rho^*=1.02$. Note that, in the absence of mode coupling $\phi(q,t)$ decays as a diffusive mode with the rate being determined by the bare shear viscosity. The result here shows the existence of shear waves[21] at finite wave numbers in a dense fluid as a consequence of mode-coupling effects.

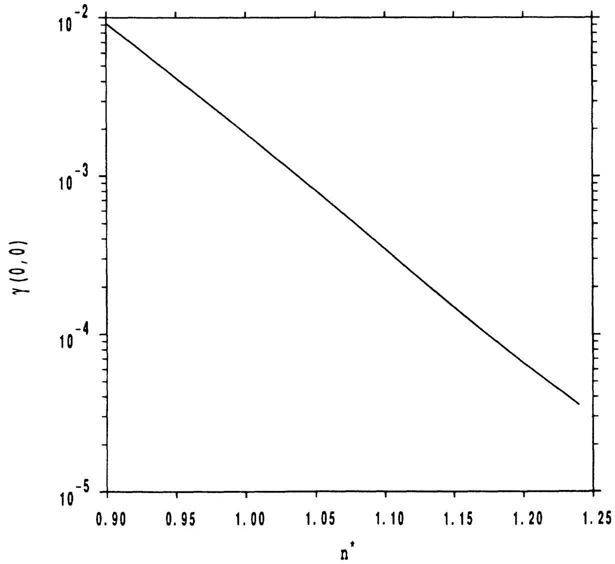

FIG. 5. $\gamma(0,0)$ vs density of the hard-sphere fluid.

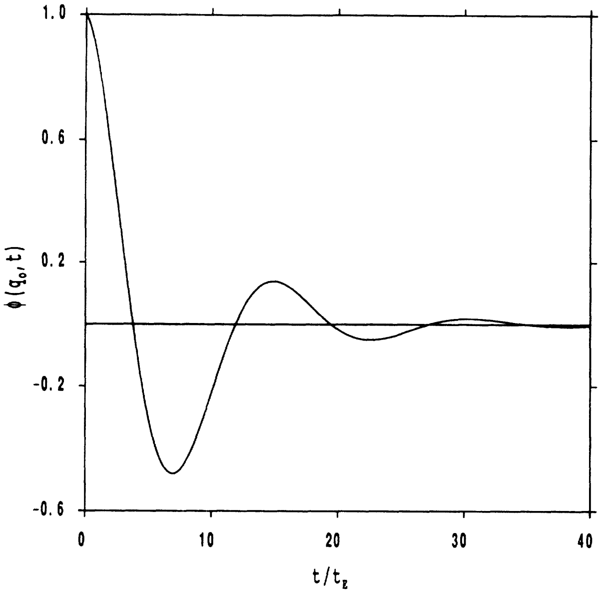

FIG. 6. The normalized transverse-current correlation function $\phi(q_0,t)$ for the hard-sphere fluid at $q_0\sigma=1.0$ and $n^*=1.02$.

So far, we have reported only the results for a hard-sphere system. These results are typical of what is observed in dense fluids. However, in order to apply the theory to more specific systems, we need to compute the proper static structure factor. In Sec. IV B we will compare the predictions of the theory with computer simulations done with a one-component Lennard-Jones fluid.

B. Lennard-Jones fluid

Ullo and Yip have done the computer simulations on a truncated Lennard-Jones potential given by

$$V(r)=\begin{cases}4\varepsilon[(\sigma/r)]^{12}-(\sigma/r)^6]+\varepsilon & \text{for } r\le r_0\\ 0 \ \text{ for } r>r_0\end{cases}$$

where $r_0=2^{1/6}\sigma$. σ has the dimension of length and ε has that of energy. Thus the potential is purely repulsive. In order to compute the equilibrium structure factor for such a system, we replace it by a trial hard-sphere system of diameter d ($\le 2^{1/6}\sigma$). The structure factor for the actual system can be expressed approximately in terms of that for this trial system, as follows:

$$\chi_{\rho\rho}(q)=\chi^T_{\rho\rho}(q)+\rho_0\int d^3r\, f(r)e^{-i\mathbf{q}\cdot\mathbf{r}}\ , \tag{38}$$

where

$$f(r)=g_T(r)e^{\beta V_d(r)}(e^{-\beta V(r)}-e^{-\beta V_d(r)}) \tag{39}$$

and $g_T(r)$ is the pair distribution function for the trial hard-sphere system described by the potential $V_d(r)$. The hard-sphere diameter d in the trial system is an open parameter and it is adjusted so that the compressibility for the original and the trial systems are equal.[13] Once d is known, the static structure for this system can easily be computed. Also, for this purely repulsive system we take the bare transport coefficients to be equal to that for this trail hard-sphere system. We have used the Carnahan-Starling[22] equation for the compressibility factor of the reference hard-sphere system. The unit of time τ for the LJ system is given by $\tau=(m\sigma^2/\varepsilon)^{1/2}$ and we use the usual[8] expressions for reduced temperature $T^*=k_BT/\varepsilon$ and reduced density $n^*=n\sigma^3$.

In Fig. 7 we show how the density correlation function $\psi(q,t)$ for the LJ fluid behaves with time at a temperature $T^*=0.60$ and density $n^*=0.98$. On the same figure we also show the results obtained from Eq. (34) where the cutoff γ is ignored. This result clearly indicates that the cutoff mechanism is very important in justifying the simulation results. It is useful to note also that in the simple mode-coupling model, the LJ system undergoes the so-called ideal glass transition[4] at a density $n^*=0.965$ and $T^*=0.6$. Next, in Figs. 8 and 9 we show the time dependence of $\psi(q,t)$ for higher densities, $\rho^*=1.02$ and 1.10, respectively. The temperature is kept fixed at $T^*=0.6$. Also on the same figures we show the corresponding results from computer simulations. Although the cutoff mechanism is effective in keeping the system ergodic at high densities, the relaxation time becomes very large due to the mode-coupling effect.

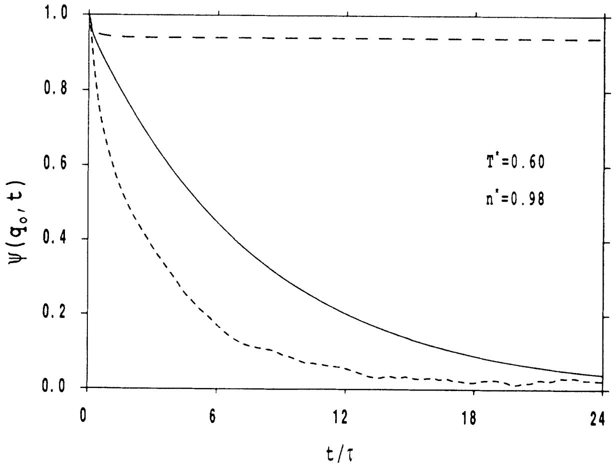

FIG. 7. The normalized density correlation function ψ vs reduced time at $q_0\sigma=6.82$ for a LJ fluid at $T^*=0.60$ and $n^*=0.98$. The solid line is the result from the present work, the long dashed line is from the simple mode-coupling theory, and the dashed line is the computer-simulation data.

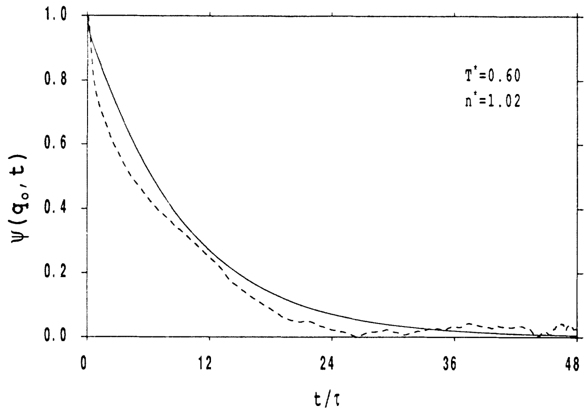

FIG. 8. $\psi(q_0,t)$ for $T^*=0.60$ and $n^*=1.02$, q_0 being same as in Fig. 7. The solid line is the present work, and the dashed line is the computer simulation.

V. DISCUSSION

We have considered here the self-consistent mode-coupling theory for dense fluids and its implications for the liquid-glass transition. The basic dynamic mechanism considered here was originally introduced in Ref. 5 by Das and Mazenko. In the present paper we have incorporated the proper equilibrium structure for the fluid in the theory, in order to compare its predictions with results from molecular-dynamics simulations. The analysis involved a self-consistent mode-coupling theory with the relevant nonlinearities for a compressible liquid taken into account. We have showed here that if we ignore terms that are higher order in wave number, we obtain from our model results similar to earlier works, i.e., a sharp transition of the fluid to a nonergodic phase above a critical density. Next we solved the complete model to show that there exists a cutoff mechanism mainly due to nonlinear couplings between density fluctuation and currents in the compressible fluid. It removes the sharp transition described above. However, there is some remnant of the transition, and the relaxation times in the fluid get longer with the increase of density. We performed our analysis for a hard-sphere system as well as for a one-component Lennard-Jones system. The upper cutoff of wave-vector integration is kept fixed at $k\sigma=25$ in all the calculations. For a hard-sphere system we show how the relaxation becomes slower with the increase of fluid density. We compute the longitudinal and shear viscosities, taking into account the mode-coupling contributions. It is found that for intermediate densities the viscosity diverges as a power-law with an exponent $\alpha=2.0$ but for very high densities the sharp divergence is

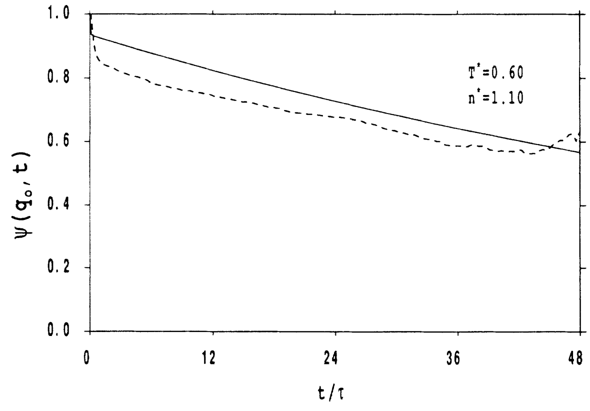

FIG. 9. Same in Fig. 8, for $T^*=0.60$ and $n^*=1.10$.

cut off and viscosity increases at a slower rate. We also compute the diffusion coefficient for the dense fluid using the Stokes-Einstein relation. The results obtained are close to those reported by Angell and Woodcock for molecular-dynamics simulation of a hard-sphere fluid for supercooled densities. We show the decay of transverse-current correlation in the fluid demonstrating the existence of shear waves at finite wave numbers due to mode-coupling effects. For a Lennard-Jones system, we have used the proper static structure factor which is an input in solving the mode-coupling equations. The results for the density autocorrelation function show good agreement with those from the molecular-dynamics simulation by Ullo and Yip. Here, we also indicate the result obtained from the simpler mode-coupling theory, which, it seems, gives rise to a too-enhanced effect.

Our results here demonstrate how the cutoff mechanism obtained in Ref. 5 affects the dynamical behavior of a dense fluid and they are in agreement with computer simulations done on similar systems. The results are qualitatively similar to the weak power-law behavior of the viscosity seen in a large number of laboratory systems as well as computer fluids over an intermediate-temperature regime than is usually associated with the glass transition. However, it is clear at this point that while such mechanisms result in considerable slowing down of transport in the dense fluid, they do not give rise to extremely slow relaxation observed in more complex systems. It is likely that such relaxation is related to the development of energy barriers in the supercooled liquid and the transport in such systems is an activated process. Identification of the proper dynamic property[23] for the fluid that is sensitive to such processes is necessary for this purpose.

The present theory illustrates how coupling of density fluctuations is effective in slowing down transport processes in a dense fluid. It indicates the importance of collective processes or correlated collisions in the dense fluid for its dynamical properties. Although the basic mechanism that is responsible for slow relaxation is essentially dynamic, the quantitative effect is very much dependent on the structure of the fluid. Thus with the increase of density the decay of dynamic correlation gets slower and produces a stronger feedback effect on the transport coefficients. But in a compressible fluid the current is also coupled to the density fluctuations. In the model described in Ref. 5 this was taken into account through the nonlinear constraint (2.1). The cutoff mechanism then follows naturally from the appropriate field-theoretical analysis. In the present work we have demonstrated how strongly it influences the dynamical behavior of the fluid at supercooled densities and that is shows reasonable agreement with computer-simulation results. However, in order to obtain results that are definitive in a strictly quantitative sense, it will be necessary to compute the correction to the linear dynamics from a nonperturbative approach.

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