Growing length scale related to the solidlike behavior in a supercooled liquid

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The behavior of propagating shear waves in a supercooled liquid is analyzed, taking into account the proper structural effects at high density. The longest wavelength for the propagating shear waves that the undercooled liquid can sustain grows with density. This length scale, which is linked to a characteristic solidlike behavior of the supercooled liquid, follows a power-law divergence with an exponent 1.2 in the vicinity of the ideal glass transition instability of the self-consistent mode-coupling theory. [S1063-651X(98)07005-6]

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The nature of the glass transition has been widely investigated in recent years from mainly two different approaches, the kinetic models [1] and the quasiequilibrium models [2–4] where an underlying continuous phase transition in the supercooled liquid results in its freezing into a solidlike amorphous state. However, the search [5,6] for a correlation length associated with any possible thermodynamic transitions has so far produced negative results. In the kinetic approach, the widely studied model [7] is obtained from a self-consistent mode-coupling approximation of the memory function in terms of the slowly decaying density fluctuations. This model has a dynamic instability characterized by the divergence of the viscosity and transition of the supercooled liquid to an ideal glassy phase beyond a critical density. The structure of the liquid does not undergo any drastic change in this transition. In the ideal glassy phase the density correlation function freezes to a nonzero long-time limit. The ideal glassy phase has solidlike properties and it can support propagating shear waves.

When a low-density fluid is sheared it does not sustain the shear and the stress is proportional to the shear rate, while in an elastic solid the stress is proportional to the strain. The viscoelastic response of the supercooled liquid is formulated in terms of the combination of the above two behaviors and the solidlike nature of the medium is reflected through the propagating shear waves. Theories of liquid state that include only the short time or uncorrelated collisions [8,9] in a liquid therefore do not account for the propagating shear waves. By considering the cooperative nature of the dynamics in a dense liquid through the mode-coupling terms in the memory function [10–12], the propagating shear waves at large enough wave numbers are accounted for.

The mode-coupling model with a glass transition as referred to above also has been derived from similar approximations. With extended mode-coupling models [13–15] it has been shown that the dynamic transition is removed. However, the complete analysis still predicts a qualitative change in the dynamics around a temperature range higher than the calorimetric glass transition temperature. This is a signature of a dynamic instability that is present in the simple model and such behavior has indeed been observed in a number of different systems such as fragile liquids from light scattering and neutron scattering studies. In the present work we analyze the behavior of the shear waves close to the transition point approaching from the liquid side.

The simplest models of undercooled liquids mainly study the dynamics of the conserved densities such as mass, momentum, and energy. There have also been attempts [16–18] to extend the set of slow modes to include properties more specific to the solidlike nature of the amorphous state. The relaxation of a shear in a fluid is studied by analyzing the transverse autocorrelation function and in the low-density fluid this correlation function is characterized by a simple pole signifying a diffusive process. For the dense fluid at small enough length scales (i.e., large enough wave numbers) it is a damped oscillatory mode, referred to as the shear waves [19,20]. We investigate here the dynamics of the transverse autocorrelation function by including in the corresponding memory function the generalized shear viscosity [21], the so-called mode-coupling term, which accounts for the cooperative dynamics at high densities. The role of structural effects on the slowing down in relaxation near the instability is determined from the wave-vector dependence [22] of the mode-coupling contributions in the theory. We have considered here a simple model for the structure of the liquid, but the results obtained here should be more generic.

The dynamics of the transverse autocorrelation function $\phi(q,t)$ [21] normalized with respect to the equal time value is given by

$$\dot{\phi}(q,t)+\eta_0(q)\phi(q,t)+\int_0^t \eta_{mc}(q,t-\tau)\phi(q,\tau)d\tau=0, \tag{1}$$

where the memory function [20] $\eta(q,t)$ corresponds to the transverse part of the viscosity tensor, giving the shear viscosity. Usually, $\eta(q,z)=\eta_0+\eta_{mc}(q,z)$, where η_0 is the short time or bare part, arising from uncorrelated binary collision of the fluid particles. The mode-coupling contribution for η_{mc} takes into account the cooperative effects in the dense fluids and has contributions from the coupling of the hydrodynamic fields. In the supercooled liquid the density fluctuations are considered to be dominant and η_{mc} is expressed self-consistently in terms of the density autocorrelation functions. The Laplace transform of the density correlation function $G_{\rho\rho}(\vec{q},t)$ normalized with respect to its equal time value can be expressed in the form [13]

$$F(\vec{q},z)=\frac{z+i\Gamma^R(q,z)}{z^2-\Omega_q^2(q)+iz\Gamma^R(q,z)}, \tag{2}$$

where $\Omega_q=q/\sqrt{\beta m S(q)}$ corresponds to a characteristic microscopic frequency for the liquid state dynamics. The corresponding memory function, the generalized longitudinal viscosity $\Gamma^R(q,z)=\Gamma_0(q)+\Gamma_{mc}(q,z)$, has a part Γ_0 related to bare or short-time dynamics with uncorrelated collisions and the mode-coupling contribution Γ_{mc} signifying the cooperative motions in the dense liquid. In the simplest approximated form the renormalized expressions for the longitudinal and shear viscosities are respectively given by

$$\Gamma_{mc}(q,t)=\lambda_0\int\frac{d\vec{k}}{(2\pi)^3}[\{\hat{q}\cdot\vec{k}\}c(k)+\{\hat{q}\cdot(\vec{q}-\vec{k})\}\times c(|\vec{q}-\vec{k}|)]^2G_{\rho\rho}(\vec{q}-\vec{k},t)G_{\rho\rho}(\vec{k},t) \tag{3}$$

and

$$\eta_{mc}(q,t)=\lambda_0\int\frac{d\vec{k}}{(2\pi)^3}[c(k)-c(\vec{q}-\vec{k})]^2k^2(1-u^2)\times G_{\rho\rho}(\vec{q}-\vec{k},t)G_{\rho\rho}(\vec{k},t), \tag{4}$$

where $\lambda_0=(2\beta m^4\rho_0)^{-1}$ and $u=\hat{q}\cdot\hat{k}$, the dot product of two corresponding unit vectors. Equations (3) and (4) are obtained from a field-theoretic analysis of the equations of nonlinear fluctuating hydrodynamics [13] for the conserved densities $\{\psi_i\}$ in the supercooled liquids, expressed in the form of generalized Langevin equations [23]

$$\frac{\partial\psi_i}{\partial t}=V_i[\psi]-\sum_j L_{ij}\frac{\delta F}{\delta\psi_j}+\theta_i. \tag{5}$$

V_i represents the reversible part of the dynamics and is usually expressed in terms of the Poisson brackets [24] between the slow variables. L_{ij} corresponds to the bare transport coefficients giving rise to dissipation. θ_i is the Gaussian random white noise that is related to the bare transport coefficients

$$\langle\theta_i(\vec{x},t)\theta_j(\vec{x}',t')\rangle=2\beta^{-1}L_{ij}\delta(\vec{x}-\vec{x}')\delta(t-t'). \tag{6}$$

The quantity F is the free-energy functional having two parts $F=F_K+F_U$. For the kinetic part F_K the standard form [25] is used, while for the potential part F_U the simple choice is in terms of the direct correlation function $c(x)$ [26],

$$F_u[\rho(x)]=\int d^3x\ \rho(x)\{\ln[\rho(x)/\rho_0]-1\}-\frac{1}{2\beta m^2}\int d^3x\ d^3x'c^{(2)}(x-x')\delta\rho(x)\delta\rho(x'), \tag{7}$$

where $\beta=1/k_BT$. Use of the form (7) obtains the results (3) and (4). For small q both $\eta(q,t)$ and $\Gamma(q,t)$ are proportional to q^2, following the Navier-Stokes hydrodynamics.

We solve for the time evolution for the transverse correlation function $\phi(q,t)$ for q small, with a self-consistent evaluation of the density correlation function $G(\vec{q},t)$ from Eq. (2). It has been demonstrated that for densities above a critical value n_c the density autocorrelation function freezes [7] to a nonzero value, i.e., $F(\vec{q},t\to\infty)=f(q)$. For a hard-sphere system whose static structure factor is approximated with the Percus-Yevick [27] (PY) solution with the Verlet-Weiss (VW) [28] correction this take place at a critical value of the packing fraction $\Delta_c=0.525$ [22]. An analysis [21] of the pole structure of the Laplace transform of Eq. (1) shows that there is dispersion relation of the form $z\sim\pm cq$ for all values of the wave vector $q\to0$. Thus the ideal glassy phase will sustain shear waves at all length scales. The speed of the shear waves c can easily be computed in terms of the $f(q)$'s [29]. Here we focus our analysis on the densities below the critical density corresponding to the dynamic instability signifying a transition to the ideal glassy phase. Although the appearance of solidlike behavior in the dense fluid arises from the cooperative nature of the dynamics expressed in terms of the mode-coupling terms, the wave-vector-dependent bare transport coefficients are also important for the short-time dynamics over different length scales, especially at short distances. In the present calculation we use for the bare transport coefficients results obtained from hard-sphere models [30], where $\Gamma_0(x)$ and $\eta_0(x)$ are respectively expressed as $(2/3t_E)[1-j_0(x)+2j_2(x)]$ and $(2/3t_E)[1-j_0(x)-j_2(x)]$, with $x=q\sigma$ being the wave vector q in terms of the hard-sphere diameter σ and j_l the spherical Bessel function of order l. t_E is the Enskog collision time [20].

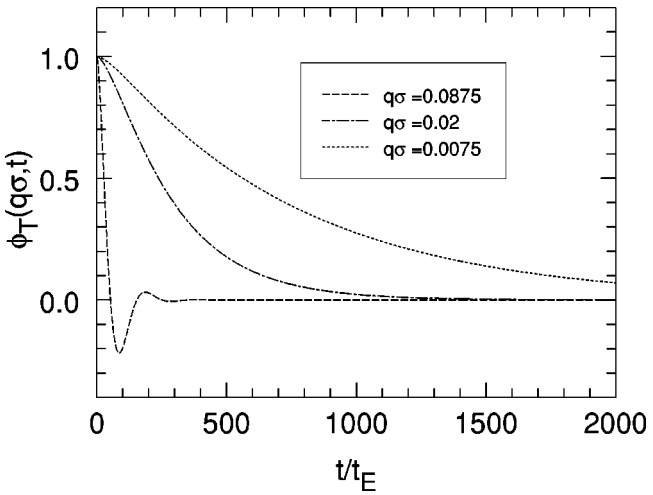

FIG. 1. Transverse current-current correlation function for $\Delta=0.450$ at values of $q\sigma=0.0075$ (dotted curve), 0.02 (dot-dashed curve), and 0.0875 (dashed curve).

We observe that for $q>q_0$ the relaxation of transverse current correlation is oscillatory, indicating that the system sustains shear waves up to this wave number. For wave vectors smaller than q_0 the decay of the correlation function is no longer oscillatory and ϕ never goes negative. In Fig. 1 we show the behavior $\phi(t)$ obtained from a self-consistent solution of the coupled set of equations (1) and (2) showing the crossover in the behavior beyond the wave vector $q\sigma=0.025$ for the packing fraction $\Delta=0.450$. In order to make a quantitative estimate of the crossover wave number we have adopted the following procedure: The mode-coupling

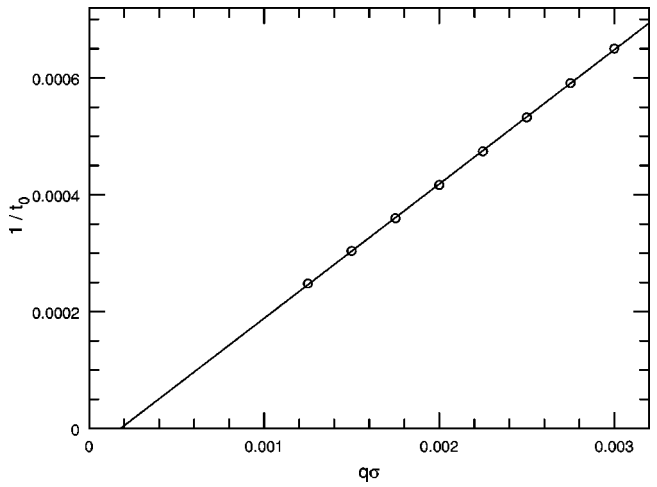

FIG. 2. Inverse of the time t_0 scaled with respect to the Enskog time t_E vs $q\sigma$ (see the text).

equations are solved for small wave vectors and an inverse of the time t_0 for which the first zero in the transverse autocorrelation function appears is plotted against the corresponding q value. In Fig. 2 this plot is shown for packing fraction $\Delta = 0.520$. For small q this shows a straight-line behavior, which corresponds to the fact that the argument of the oscillatory part in the correlation function follows $cqt_0 = \text{const}$ at the crossover to a negative value. This straight line, however, meets the q axis at a nonzero value, indicating the largest q for which an oscillatory decay of the correlation function persists. The slope of this line is proportional to the speed c of the shear wave in the dense liquid at the corresponding density. We define a length $L_0 = 2\pi/q_0$ corresponding to this critical value of the wave number for the shear wave and study its behavior as one approaches a critical density of the mode-coupling instability. In Fig. 3 the variation of L_0 with packing fraction Δ is shown for a system of hard spheres. Here we have used the PY solutions with VW corrections for the static structure factor of the liquid. As the critical packing fraction 0.525 is approached the observed length scale indicates a divergence of the length scale L_0. Very close to the

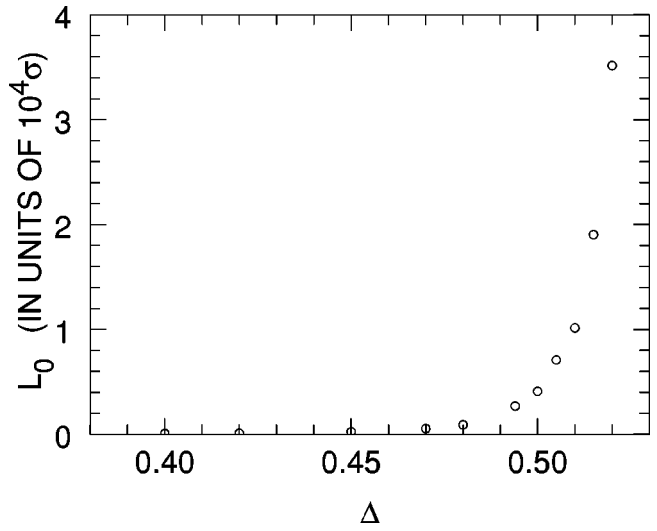

FIG. 3. Growth of the length scale L_0 (defined in the text) with the packing fraction Δ.

critical density the results fit well to a power-law divergence form with an exponent of 1.2.

We have considered here the simple form of the mode-coupling kernel that results in a sharp transition of the supercooled liquid to an ideal glassy phase beyond a critical density. With extended mode-coupling models [13,14] one should expect the removal of any sharp divergence in L_0 as the critical packing fraction Δ_c is approached. Such theories have demonstrated that in the final decay process ergodicity is restored in the supercooled liquid over the longest-time scale and hence rules out any transition to an ideal glassy phase with infinite viscosity. However, the dynamic instability predicted by the simple mode-coupling model is not an artifact of the approximation. Strong remnants of the transition are seen in the study of supercooled liquid dynamics and this has led to identification of a different temperature T_c, signifying a qualitative change in the dynamics of the supercooled liquid. It has been shown in very widely investigated studies in recent years that in experiments [31–33] and computer simulations [34] at the supercooled densities for a class of systems referred to as fragile glasses, signatures of such a transition temperature can indeed be identified. We have investigated here the implications of the simple model as a first step towards understanding the growing length scales in a supercooled liquid. A complete picture should emerge with the consideration of the extended mode-coupling model. For a full analysis of the growth behavior of the length scale, using the extended model, one would be required to have a better understanding of the short-wavelength behavior of the correlation function. Indeed, the length scale L_0 does not represent any underlying thermodynamic phase transition, but indicates how the cooperative nature of the dynamics of structural relaxation, accounted for through the mode-coupling terms, grows with the density and is affected by the dynamic instability of the ideal glass transition. The solidlike nature of undercooled liquids has also been observed from the transverse sound modes [35]. Mountain has observed [36] a similar behavior of propagating shear waves from molecular-dynamics simulations of fragile liquids, which are also the systems where the mode-coupling models apply. This length scale of maximum wavelength for propagating shear waves observed from molecular-dynamics simulations grows indefinitely, approaching the glass transition. In the present work we have demonstrated that for the self-consistent mode-coupling model this length scale follows a power-law divergence around its characteristic dynamic instability.

We like to stress here the importance of our work with reference to a viscoelastic theory. In a viscoelastic theory a phenomenological parameter is introduced to describe a frequency-dependent shear viscosity and using a simple exponential time dependence in the transport coefficient one can obtain propagating shear waves in terms of this relaxation parameter. However, whether or not it has anything to do with the growing length scales in a supercooled liquid *can only be investigated by using experimental data as an input in these models*, be it real or computer experiment. On the other hand, we have considered a theoretical model that is obtained from first principles. It includes as an input only the static structure factor of the *liquid*. The identical model has already been used by various authors to investigate other

aspects of the supercooled liquid dynamics. The growing length scale follows very naturally from the feedback of density fluctuations and *without any diverging parameters being used as an input*.

We also like to stress the importance of the proper wave-vector dependence in the model reflecting the effects of structure on the dynamics. Since the relaxation time is inversely proportional to the shear modulus, it follows quite easily that beyond the ideal glass transition point there is propagating shear waves at all length scales. This is related to the diverging shear viscosity reflecting an elastic behavior at all length scales in the ideal glassy phase, a result that follows from the mode-coupling theories predicting a diverging shear viscosity. However, in the present analysis of the divergence of the length scale L_0, as one approaches the instability from the liquid side, the wave-vector dependence of the shear modulus related to the solidlike behavior is necessary. The length scale L_0 is related to the dynamic behavior of the system and is representative of the distance over which the supercooled liquid do have enough structure to sustain propagating shear waves.

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