Elastic behavior in a supercooled liquid: Analysis of viscoelasticity using an extended mode coupling model

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The transverse current correlations are analyzed using the formalism of extended mode coupling theory. The undercooled liquid can sustain shear waves up to a minimum wave number. With the increase of density this wave number decreases, indicating a growing length scale that is related to the dynamics. The speed of the propagating shear waves goes to zero approaching a critical wave number. The maximum wavelength shows an initial enhancement approaching the mode coupling transition and finally grows at a slower rate as the sharp transition is cut off.

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The solidlike nature of a supercooled liquid is often expressed in terms of a finite shear modulus. Thus, while a low-density fluid cannot sustain a shear stress, in an elastic solid the stress is proportional to the strain produced. The viscoelastic response of the supercooled liquid is formulated in terms of a combination of the above two behaviors. Theories of the liquid state which only include short-time or uncorrelated collisions [1,2] in a liquid therefore do not account for the appearance of propagating shear waves. By formulating the the dynamics in a dense liquid in terms of the memory function [3–5], the propagating shear waves at large wave numbers are accounted for. More recent works [6] have considered the problem of long-time tails similar to the work by Kirkpatrick [3] with inclusion of coupling to current correlations.

The memory effect accounts for the dynamic correlations that build up at high density and are expressed by the mode coupling terms. In recent years the self-consistent mode coupling theory (MCT) [7] for glassy relaxation has been proposed by considering the contribution to the transport coefficients coming from the nonlinear coupling of collective modes in a liquid. In the kinetic approach to glassy behavior, the widely studied model is obtained from a self-consistent mode coupling approximation of the memory function in terms of slowly decaying density fluctuations. This model undergoes a dynamic transition to an ideal glassy phase beyond a critical density while the structure of the liquid does not undergo any drastic change. In the ideal glassy phase the density correlation function freezes to a nonzero long-time limit. However, a study of the equations of nonlinear fluctuating hydrodynamics [8] shows that the dynamic feedback mechanism causing a divergence of the viscosity is cut off as a result of the coupling of density fluctuations to current in a compressible fluid. In these so-called extended mode coupling models [8–11] it has been shown that the dynamic transition is removed. The relaxation times keeps increasing, but the density correlation function finally decays to zero in the long-time limit. The ideal glassy phase predicted within the simple mode coupling approximation has solidlike properties and it can support propagating shear waves at all length scales. In a recent work [12] the behavior of propagating shear waves in the supercooled liquid was analyzed, taking into account the proper structural effects at high density, through a mode coupling calculation. The extent of slowing down in relaxation near the instability is determined from the wave vector dependence of the mode coupling contributions in the theory. It was shown that 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 of 1.2 in the vicinity of the ideal glass transition density. With the proper approximation to the memory function in terms of the density correlation function computed from extended mode coupling models, the divergence of the characteristic length scale is removed.

In the formalism of the mode coupling theories the density correlation function is the key quantity in terms of which the glassy relaxation is formulated. The Laplace transform of the density correlation function $\psi(\vec{q},t)$ normalized with respect to its equal time value is defined as

$$\psi(\vec{q},z)=-i\int_0^\infty dt \quad e^{izt}\psi(q,t) \tag{1}$$

and can be expressed in the form [8]

$$\psi(\vec{q},z)=\frac{z+i\Gamma^R(q,z)}{z^2-\Omega_q^2+i\Gamma^R(q,z)[z+i\gamma(q,z)]}. \tag{2}$$

$\Omega_q=q/\sqrt{\beta m S(q)}$ corresponds to a characteristic microscopic frequency for the liquid-state dynamics where β is the Boltzmann factor and m is the mass of the fluid particles. 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 correlated motion in the dense liquid:

$$\Gamma_{mc}(q,t)=\int V^L[\vec{k},\vec{k}_1]\psi(\vec{k},t)\psi(\vec{k}_1,t)\frac{d\vec{k}}{(2\pi)^3}, \tag{3}$$

where $\vec{k}_1=\vec{q}-\vec{k}$. The vertex function for the longitudinal viscosity is given by

$$V^L[\vec{k},\vec{k}_1]=\frac{n}{2\beta m}[ukc(k)+u_1k_1c(k_1)]^2S(k)S(k_1), \quad (4)$$

where $u=\hat{q}\cdot\hat{k}$ and $u_1=\hat{q}\cdot\widehat{k_1}$, the dot product of the corresponding unit vectors. Here $c(k)$ is the direct correlation function related to the static structure factor $S(k)$ through the Ornstein-Zernike relation $S(k)=[1-nc(k)]^{-1}$. The quantity $\gamma(q,z)$ on the right-hand side (RHS) of Eq. (2) plays a crucial role in determining the asymptotic dynamics. If γ is ignored, the simple mode coupling approximation for the memory function obtains a sharp transition to an ideal glassy phase beyond a critical density, with the density correlation function developing a $1/z$ pole. This model has been widely studied [13] for the dynamics of supercooled liquids and involves a transition to an ideal glassy phase beyond a critical density. However, with the presence of γ at high density when Γ^R gets large, the pole shifts to $1/(z+i\gamma)$. It has been demonstrated [8,10] that in the small-q and -ω limit, $\gamma\sim q^2$. This gives rise to a diffusive decay of the density correlation restoring ergodicity over the longest time scale. A formal expression was obtained in Ref. [8] for the quantity γ using nonperturbative analysis. For the calculations here we use the one-loop results in the simplest form, in the small-q, ω limit:

$$\gamma(q,t)=\gamma_q^2\int\frac{d\vec{k}}{(2\pi)^3}S(k)S(k_1)\frac{u}{k}\left[\frac{u}{k}+\frac{u_1}{k_1}\right]\dot{\psi}(k_1,t)\dot{\psi}(\vec{k},t). \quad (5)$$

$\dot{\psi}$ refers to the time derivative of the function $\psi(q,t)$. Here

$$\gamma_q{}^2=\frac{1}{2n}\left(\frac{\Omega_q}{v_0}\right)^2,$$

where v_0 is the thermal speed of the particles. Here the couplings to the transverse correlations are ignored to keep the analysis simple. The quantity γ provides a mechanism that cuts off the sharp transition of the fluid to an ideal glassy phase. To leading order it is of $O(k_BT)$ and is an effect of the coupling of the density and current correlations in the compressible fluid. The shear relaxation in a fluid is studied by analyzing the transverse autocorrelation function $\phi(q,t)$ which is expressed in the Laplace transformed form

$$\phi(\vec{q},z)=\frac{1}{z+i\eta^R(q,z)} \quad (6)$$

in terms of the memory function or the generalized shear viscosity $\eta^R(q,z)=\eta_0+\eta_{mc}(q,z)$, where η_0 is the short-time or bare part arising from uncorrelated binary collision of the fluid particles. For the dense fluid at small enough length scales (i.e., large enough q) the memory effects are important; a damped oscillatory mode the shear wave [14,15] is obtained. 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 assumed to be dominant and η_{mc} is expressed self-consistently in terms of the density autocorrelation functions.

The time evolution for the transverse correlation function $\phi(q,t)$ is solved for q small, with a self-consistent evaluation of the density correlation function $\psi(\vec{q},t)$ from Eq. (2). In a simplified model where the quantity γ is ignored, the density autocorrelation function freezes [7] to a nonzero value for densities above a critical value n_c. For a hard sphere system whose static structure factor is approximated by the Percus-Yevick (PY) [16] solution with the Verlet-Weiss (VW) [17] correction this takes place at a critical value of the packing fraction $\eta^*=0.525$. We focus here our study on the densities above the critical density corresponding to the dynamic transition to the ideal glassy phase. At these densities in the simple MCT there will be complete freezing at all length scales. To investigate the nature of the shear waves at small wave numbers we compute the memory function in terms of the density correlation function that is obtained here from the extended MCT. For analyzing the nature of the shear waves the small wave vector region becomes more important with increasing density. However, in computation of the mode coupling integrals the large wave vector part contributes. $\gamma(q,t)$ is approximated here by the result given in Eq. (5) obtained both in Refs. [8] and [18]. Since the value of $\psi(\dot{q},t$ in the initial times is mainly contributing to the cutoff function, we compute the γ from the simple model without the cutoff mechanism and use its value in the hydrodynamic limit to compute the final decay of the density correlation function. For small $q\sigma\leqslant 1$, the cutoff part $q^2\gamma\sim q^2$. To compute the transverse autocorrelation function for different wave numbers we use the standard form [19,20] for the mode coupling contribution to the generalized shear viscosity or the memory function:

$$\eta_{mc}(q,t)=\frac{n}{2\beta m}\int\frac{d\vec{k}}{(2\pi)^3}[c(k)-c(\vec{k}_1)]^2k^2 \times(1-u^2)\psi(\vec{k}_1,t)\psi(\vec{k},t). \quad (7)$$

For the small wave vector an expansion in q is used to compute the memory function that is used in the calculation of the transverse autocorrelation function for different values of the wave number. From the study of the dynamics a wave number q_0 is identified such that with $q>q_0$ 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 order to make a quantitative estimate of the crossover wave number we have adopted the procedure outlined for the calculation with the simplified model [12], namely, extrapolating to zero the inverse of the time t_0 for which the transverse autocorrelation function goes negative at a given wave vector q. In Fig. 1, we show the behavior of the speed of shear waves vs wave vector for reduced density $n\sigma^3=1.08$. The unit chosen is in terms of the Enskog time t_E [15] and the hard sphere diameter σ. As the critical wave number is approached the speed of the shear waves goes to zero. For large wave number the speed of the shear wave reaches its hydrodynamic value which is equal to $\sqrt{G_\infty/\rho}$ where G_∞ is the high-frequency limit of the shear modulus. Using this limiting value of the shear wave speed we can thus compute the shear modulus [21] with the only input as the structure of the liquid. This is related [5] to the short-time

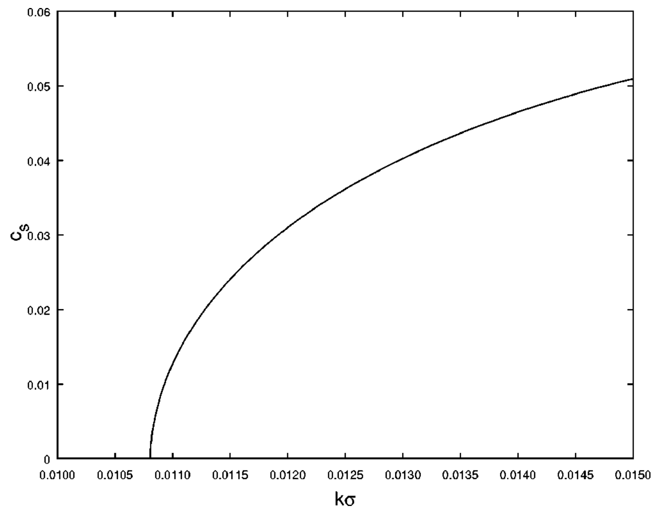

FIG. 1. The speed of shear wave in units of σ/t_E (see text) vs wave number $k\sigma$ at density $n\sigma^3=1.08$.

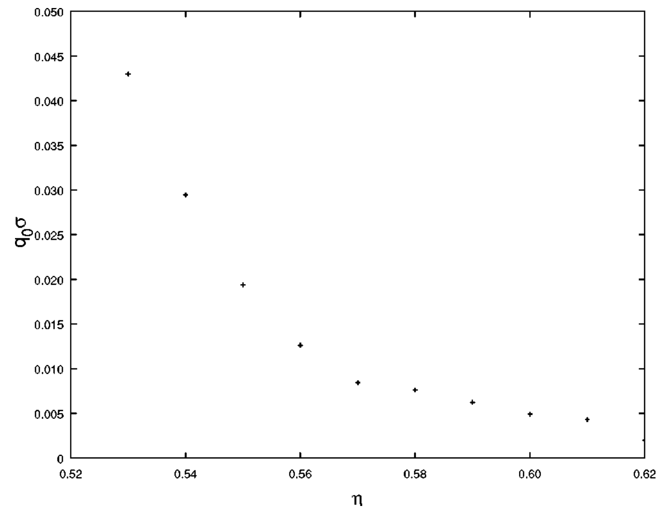

FIG. 3. The wave number q_0 (defined in text) in units of σ^{-1} vs the packing fraction η.

value of the memory function. In Fig. 2 the wave vector dependence of cutoff function $\gamma(q,0)/q^2$ is shown for the small wave vector range $q\sigma \leqslant 1$ for the packing fraction $\eta = 0.57$. The constant value refers to the diffusive mode in the hydrodynamic limit. In Fig. 3 the variation of q_0 with packing fraction $\eta(=\pi n\sigma^3/6)$ is shown for a system of hard spheres. As the critical packing fraction 0.525 is approached the observed length scale L_0 tends to diverge, with q_0 becoming small. However, as the density is further increased the approach to the sharp transition is cut off and a weaker enhancement takes place.

The solidlike nature of undercooled liquids has also been observed from transverse sound modes [22]. Mountain has observed [23] 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 such a growing length scale

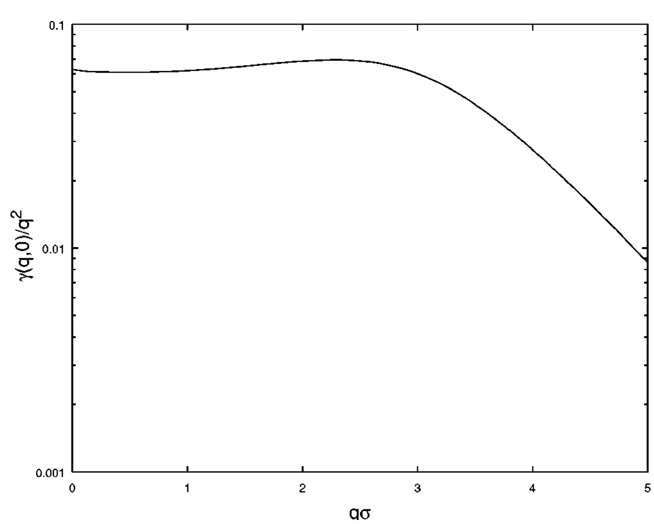

FIG. 2. The cutoff function $\gamma(q,0)/q^2$ in units of σ^2/t_E on a $\log_{10}$ scale vs wave vector $q\sigma$.

can be identified and it shows a change in its growth pattern around the mode coupling instability. For small q a value of the quantity γ has been obtained through a proper analysis of the nonlinear fluctuating hydrodynamics equations and we extrapolate this form to a large q with simple approximations to estimate it. The present version of extended MCT uses the hydrodynamic form and is being used to study the nature of the shear waves at small wave numbers. The dynamic instability that has been called the ideal glass transition is specific to the self-consistent mode coupling model. In a recent work it has been argued that the final relaxation of the density correlation is q independent. The feedback mechanism responsible for the dynamic transition is q independent—however, the exact density at which the mode coupling transition occurs is determined by the mode coupling integrals and hence the structure factor of the supercooled liquid that is used an input in the theory. In Eq. (2) when the cutoff function γ is ignored, for small q, if the viscosity is large enough so that $z \ll D(0)q^2$, the central viscoelastic peak will have a q-independent width given by $D^{-1}(0)$ where D is the viscosity divided by the density factor. However, when the mode coupling equations are solved with a realistic structure factor one sees that this width goes to zero at $\eta^* = 0.514$ [7] with a Percus-Yevick structure factor. Thus the presence of the γ term is crucial in the ergodicity restoring process over the longest time scale. It was shown in Ref. [8] that to leading order in q, $\gamma \sim q^2$, giving rise to a diffusive process in the supercooled liquid. We would also like to point out here that γ going to zero with q approaching zero is also required from hydrodynamics. The same result [18] was also obtained in Ref. [10]. Beyond the hydrodynamic regime, the central peak has a width independent of q, commonly called the Mountain peak [24], which is highly non-Lorentzian, reflects faster processes, and does not play a crucial role here. The coupling to thermal fluctuations is also ignored in the formulation with the presumption that the density fluctuations are the key quantity. We have also not taken into account the coupling to other slow modes that arises in the glass forming liquids due to the complexity of molecules or properties related to orientational degrees of freedom [25] or an explicit account of hopping processes [11]. While there can be a more involved formalism of the mode coupling terms, the present work demonstrates that the simplest mode coupling terms with density fluctuations are crucial in understanding shear waves.

The change of the nature of the shear wave indicated here is reminiscent of what happens in a dense fluid [26,27] at finite wave vectors when the propagating sound modes become diffusive. Although in the latter case it is purely a structural effect, the change of the propagating modes to a diffusive mode is qualitatively similar. In the present case the change in the nature of shear waves occurs as a result of the interplay between structure and dynamics. It is also worth mentioning at this point that it will not be correct to simply relate this to very slow transverse sound modes near wave vectors approaching the critical value. We have discussed here the shear mode from the transverse current correlation functions for an isotropic liquid. In the case of transverse sound modes, on the other hand, one needs to discuss really the transverse part of displacement fields introduced as extra slow modes or Goldstone modes [28].

In a viscoelastic theory [29] 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. On the other hand, we have considered a theoretical model which is obtained from first principles. It includes as an input only the static structure factor of the *liquid*. An identical model has already been used earlier by the present author to investigate the nature of the supercooled liquid dynamics. The growing length scale follows very naturally from the feedback of density fluctuations and *without any input parameters being used*. We have used the extended mode coupling model to investigate the wave vector dependence in the elastic response of the supercooled liquid. The length scale is related to the dynamic behavior of the system and is representative of the distance over which the supercooled liquid does have enough structure to sustain propagating shear waves.

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[1] G.F. Mazenko, T.Y.C. Wei, and S. Yip, Phys. Rev. A **6**, 1981 (1972).
[2] J.W. Dufty, M.J. Lindenfield, and G.E. Garland, Phys. Rev. A **24**, 3212 (1981).
[3] T.R. Kirkpatrick, Phys. Rev. Lett. **53**, 1735 (1984).
[4] E. Leutheusser, J. Phys. C **15**, 2801 (1982).
[5] J.P. Hansen and J.R. Mcdonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1976).
[6] T. Franosch and W. Götze, Phys. Rev. E **57**, 5833 (1998).
[7] U. Bengtzelius, W. Götze, and A. Sjolander, J. Phys. C **17**, 5915 (1984).
[8] S.P. Das and G.F. Mazenko, Phys. Rev. A **34**, 2265 (1986).
[9] W. Götze and L. Sjögren, Z. Phys. B: Condens. Matter **65**, 415 (1987).
[10] R. Schmitz, J.W. Dufty, and P. De, Phys. Rev. Lett. **71**, 2066 (1993).
[11] C.Z. Liu, and I. Oppenheim, Physica A **235**, 369 (1997); M. Manno and I. Oppenheim *ibid.* **265**, 520 (1999).
[12] R. Ahluwalia and S.P. Das, Phys. Rev. E **57**, 5771 (1998).
[13] Transp. Theory Stat. Phys. **24** (1995), special issue on glass transitions, edited by S. Yip and Paul Melman.
[14] W.E. Alley, B.J. Alder, and S. Yip, Phys. Rev. A **27**, 3174 (1983).
[15] J.P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York 1979).
[16] D. Henderson and E.W. Grundkie, J. Chem. Phys. **63**, 601 (1975).
[17] L. Verlet and J.J. Weiss, Phys. Rev. A **5**, 939 (1972).
[18] S.P. Das, Phys. Rev. E **54**, 1715 (1996).
[19] T. Munakata and A. Igarashi, Prog. Theor. Phys. **60**, 45 (1978).
[20] S.P. Das, Phys. Rev. A **42**, 6116 (1990).
[21] S.P. Das (unpublished).
[22] R.D. Mountain, J. Res. Natl. Bur. Stand., Sect. A **70**, 207 (1966).
[23] M. Grimsditch, R. Bhadra, and L.M. Torell, Phys. Rev. Lett. **62**, 2616 (1989).
[24] R.D. Mountain, J. Chem. Phys. **102**, 5408 (1995).
[25] T. Keys and D. Kivelson, J. Comput. Phys. **54**, 1786 (1972).
[26] I. de Schepper and E.G.D Cohen, J. Stat. Phys. **27**, 223 (1982).
[27] James F. Lutsko, James W. Dufty, and Shankar P. Das, Phys. Rev. A **39**, 1311 (1989).
[28] P.C. Martin, O. Parodi, and P.S. Pershan, Phys. Rev. A **6**, 2401 (1972).
[29] S.M. Rytov, Zh. Éksp. Teor. Fiz. **58**, 2154 (1970) [Sov. Phys. JETP **31**, 1163 (1970)].