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Elastic Behavior in a Supercooled Liquid - analysis of Viscoelasticity using extended mode coupling model

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ABSTRACT

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 wavenumber. 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 slower rate as the sharp transition is cutoff.

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The solid like 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 the combination of the above two behavior. Theories of liquid state which only include the short time or uncorrelated collisions [1, 2] in a liquid therefore does 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, 4, 5] , the propagating shear waves at large wavenumbers are accounted. The memory effects accounts for the dynamic correlations that build up at high density and are expressed with the mode coupling terms. In recent years the self consistent mode coupling theory (MCT) [6] 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 the 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 longtime limit. However, study of the equations of Nonlinear Fluctuating Hydrodynamics [7] shows that the dynamic feed back mechanism causing a divergence of the viscosity is cutoff as a result of coupling of density fluctuations to current in a compressible fluid. In these so called extended mode coupling models [7, 8, 9, 10] 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 longtime limit. The ideal glassy phase predicted within the simple mode coupling approximation has solid like properties and it can support propagating shear waves at all length scales.

In a recent work [11] the behavior of propagating shear waves in the supercooled liquid was analized 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 solid like behavior of the supercooled liquid, follows a power law divergence with an exponent 1.2 in the vicinity of the ideal glass transition density. In the present paper we consider the extended mode coupling model where any transition to an ideal glassy phase is absent and the density correlation that contributes to the mode coupling effects decays to zero in the long time limit. With the proper approximation to the memory function essential for the dynamics of shear waves, the divergence of the characteristic length scale is removed.

The shear relaxation in a fluid is studied by analyzing the transverse auto correlation function. The nature of the dynamics is usually expressed in terms of the Laplac transform [12] and the corresponding poles in the complex z plane. The transverse autocorrelation function $\phi(q,t)$ normalized with respect to its equal time value can be expressed in the Laplac transformed form, [12]

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

in terms of the memory function or the generalized shear viscosity $\eta^R(q,z)$. In the low density fluid, where the collisions are random, memory effects are negligible giving an η^R which is independent of frequency z. In this limit, $\phi(q,z)$ has a simple pole [12] signifying a diffusive process. 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 [13, 14] is

obtained. The dynamics of the transverse autocorrelation function is then expressed in terms of the corresponding generalized shear viscosity [12] $\eta(q,z) = \eta_0 + \eta_{mc}(q,z)$, 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 assumed to be dominant and η_{mc} is expressed self consistently in terms of the density auto correlation functions. In the formalism of the mode coupling theories 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 can be expressed in the form, [7]

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

$\Omega_q = q/\sqrt{\beta m S(q)}$ 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 $\vec{k_1} = \vec{q} - \vec{k}$. $u = \hat{q}\cdot\hat{k}$, the dot product of two corresponding unit vectors. The vertex function for the longitudinal viscosity is given by,

$$V^L[\vec{k},\vec{k_1}] = \frac{n}{2\beta m}[ukc(k) + u_1 k_1 c(k_1)]^2 S(k)S(k_1) \tag{4}$$

where $u_1 = \hat{q} \cdot \hat{k_1}$ and $c(k)$ 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 $\gamma(q, z)$ in the R.H.S of eqn. (2) plays a crucial role in determining the asymptotic dynamics. If γ is ignored the simple mode coupling approximation for memory function obtains the 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 [15] for the dynamics of supercooled liquids and involves 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 $1/(z + \gamma)$. It has been demonstrated [7, 9] that in the small q and ω limit, $\gamma \sim q^2$. This give rise to a diffusive decay of the density correlation restoring ergodicity in the longtime limit. Formal expression was obtained in ref. [7] for the quantity γ using nonperturbative analysis. For calculations here we use the one loop results in the simplest form, in the small q, ω limit.

$$\gamma(q, t) = \gamma_o q^2 \int dk [\dot{\psi}(k, t) S(k)]^2 \tag{5}$$

$\dot{\psi}$ refers to the time derivative of the function $\psi(q, t)$ and $\gamma_o = {v_o}^2/(6n\sigma^2\pi^2)$, v_o being the thermal velocity of the particles. The quantity γ provides a mechanism that cuts off the sharp transition of the fluid to an ideal glassy phase. It is $O(k_B T)$ to leading order is an effect of the coupling of the density and current correlations in the compressible fluid and gives rise to a diffusive process whereby complete freezing of the dynamic correlations in density fluctuations are smoothed.

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 $\psi(\vec{q}, t)$ from the equation (2). It has been demonstrated [16] that in a simplified model where the quantity γ coming from the coupling of currents to the density fluctuations is ignored,

the density auto correlation function freezes [6] to a nonzero value for densities above a critical value n_c. For a hard sphere system whose static structure factor is approximated with the Percus-Yevick[17] (PY) solution with the Verlet-Weiss (VW) [18] correction this take place at a critical value of the packing fraction $\eta^* = .525$ [19]. We focus here our study for 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. The wave vector dependent bare transport coefficients in the equations of motion for ϕ are relevant for the short time dynamics over different length scales specially at short distances. In the present calculation we use for the bare transport coefficients relevant for the short tyme dynamics the results obtained from hard sphere models [20] with $\Gamma_0(x)$ 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. j_l the spherical Bessel function of order l and t_E the Enskog collision time [14]. To investigate the nature of the shear waves at small wave numbers we compute the memory function in terms of the density correlation function. In the present calculation the later is obtained from the extended MCT computation over a wide range of wave vectors, from small up to a cutoff value. The extended mode coupling model that is used here does obtain a form of the cutoff function in the hydrodynamic limit. Indeed for analyzing the nature of the shear waves the small wave vector region become more important with increasing density. However, in computation of the mode coupling integrals the large wave vector part contributes. For small wave numbers as was indicated above there is a diffusive mode restoring ergodicity. We choose the cutoff function giving a diffusive pole by approximating $\gamma(q,t)$ by the hydrodynamic limit given in (5) value. We assume that the the cutoff function is constant [21] beyond $q\sigma = .015$ around which value of the wave vector $q\sigma$ the structure factor which is the only in put in the present

theory reaches within one percent of its hydrodynamic limit. For the density range of interest here we use this as the cutoff value for using the hydrodynamic expression for γ. To compute the transverse auto correlation function for different wave numbers we use the standard form for the mode coupling contribution to the generalized shear viscosity or the memory function.

$$\eta_{mc}(q,t) = \frac{n}{2\beta m}\int \frac{d\vec{k}}{(2\pi)^3}\Big[c(k)-c(\vec{k_1})\Big]^2 k^2(1-u^2)\psi(\vec{k_1},t)\psi(\vec{k},t) \tag{6}$$

For small q expression this obtains up to quatric order,

$$\eta_{mc}(q,t) = \frac{1}{\beta m}\int [q^2 {V_T}^{(0)} + q^4 {V_T}^{(2)} + ...][\psi(\vec{k},t)S(k)]^2 \frac{dk}{40\pi^2} \tag{7}$$

where the vertex functions V^T's are respectively given by, $V^{(0)} = \frac{2}{3}k^4 c'^2(k)$ and $V^{(2)} = \frac{k^2}{7}[4c'^2(k) - \frac{4}{3}kc'(k)c''(k) + \frac{k^2}{2}c''^2(k)]$. We make detailed calculation of the transverse auto correlation function for different values of the wave number and study the nature of its relaxation with time. ¿From the study of the dynamics a wave number q_o is identified such that with $q > q_o$ 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_o the decay of the correlation function is no longer oscillatory and ϕ never goes negative. In order to make a quantitative estimate of the cross over wavenumber we have adopted the procedure outlined for the calculation with the simplified model [11], namely extrapolating to zero the inverse of the time t_o for which the transverse autocorrelation function goes negative at a given wave vector q. We define a length $L_o = 2\pi/q_o$ corresponding to this critical value of the wave number for the shear wave which corresponds to the maximum wavelength for propagating shear waves.

In figure 1 the transverse auto correlation function is showed for the packing fraction

$\eta = .57$ As the wave number is decreased we see that the nature of time relaxation of the transverse correlation function changes from a propagating to an exponential decay. Thus at a given density, as the critical wavenumber is approached the propagating shear mode transforms to a diffusive mode reflecting the liquid like behavior. For $q > q_o$ the speed of the propagating shear waves are computed from the decay of the time correlation function. In figure 2, we show the behavior of the speed of shear waves vs. wave vector for reduced density $n\sigma^3 = 1.08$. 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 and the result is shown in figure 3. This is related [5] to the short time value of the memory function. The only input in the present calculation comes from the structure of the liquid. In Figure 4 the variation of q_o with packing fraction η ($= \pi n\sigma^3/6$) is shown for a system of hard spheres. As the critical packing fraction .525 is approached the observed length scale L_o tends to diverge, with q_o becoming small. However as the density is further increased the approach to the sharp transition is cutoff for a less severe enhancement takes place.

Indeed, the length scale L_o does not represent any underlying thermodynamic phase transition but indicates how the cooperative nature of the dynamics of structural relaxation accounted through the mode coupling terms, grows with the density and is affected by the dynamic instability of ideal glass transition. Solid like nature of undercooled liquids have also been observed from the transverse sound modes [23]. Mountain has observed [24] 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 can be identified and it shows a change in its growth pattern around the mode coupling instability. We have used the expression (5) for small wave vectors by having a diffusive mode that comes out of the collective dynamics at supercooled densities. While the small q value of the quantity γ has been obtained through a proper analysis of the NFH equations, we extrapolate this form to large q using simple approximations to estimate it. The large q behavior which should involve large wave vector extension of the mode coupling formalism going beyond the simple one loop approximation [10] to investigate the hopping motion in the supercooled liquid. The present version of extended MCT is using the hydrodynamic form and being used to study the nature of the shear waves at small wave numbers. It has been established by independent works [7, 9] that in the small wave q limit, the final decay process restoring ergodic behavior in the density auto correlation function is diffusive. Beyond the hydrodynamic regime, the central peak has a width independent of q, commonly called the Mountain Peak [21] which is highly non-Lorentzian, reflects faster processes and does not play a crucial role here. The coupling to thermal fluctuations are also ignored in the formulation with the presumption that the density fluctuations are the key quantity. We have also not taken in to account coupling to other slow modes that arises in the glass forming liquids due to complexity of molecules or properties related to orientational degrees of freedom [25]. While there can be 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.

In a viscoelastic theory [26] 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*. The 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 feed back 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 L_o 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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Figure Captions

Figure 1

The normalized transverse current-current correlation function $\phi(q,t)$ for $q\sigma$= .0025 (solid), .0035 (dashed), .0040 (dot-dashed) and .005 (dotted), at $\eta = .57$.

Figure 2

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

Figure 3

The shear modulus G_∞ in units of $(k_B\mathrm{T})/\sigma^3$ (on a $\log_{10}$ scale) vs. packing fraction η.

Figure 4

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

Table 1

The Length scale L_o in units of σ for different values of the packing fraction η.

η	L_o
0.49	257.30
0.50	415.28
0.51	574.86
0.52	874.97
0.53	1120.20
0.54	1267.80
0.55	1411.95
0.56	1590.67
0.57	1841.50
0.58	2203.85
0.59	2918.34
0.60	4390.77
0.61	7486.22

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