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2000 J. Phys.: Condens. Matter 12 6423

(http://iopscience.iop.org/0953-8984/12/29/314)

J. Phys.: Condens. Matter **12** (2000) 6423–6430. Printed in the UK PII: S0953-8984(00)13004-8

Dynamic length scales and feedback from long-time structural relaxation in a simple liquid

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Received 3 April 2000

Abstract. Liquid can sustain shear waves up to a minimum wavenumber, indicating solid-like behaviour over short length scales. With the increase of density this critical wavenumber decreases, indicating a growth of a dynamic length scale. The speed of the propagating shear waves goes to zero approaching a critical wavenumber. 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. The growth of this dynamic length scale in the supercooled regime is studied using the transverse correlation function and by computing the feedback effects of dynamic correlation in an extended mode-coupling model where the structure factor of the liquid is used as an input.

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 behaviours. Theories of the liquid state which only include the short-time or uncorrelated collisions [1, 2] in a liquid therefore do not account for the appearance of propagating shear waves. By formulating the dynamics in a dense liquid in terms of the memory function [3–5], the propagating shear waves at large wavenumbers are accounted for. The memory effects account for the dynamic correlations that build up at high density and are expressed as mode-coupling terms. In recent years, the self-consistent mode-coupling theory (MCT) [6] for glassy relaxation has been proposed, considering the contribution to the transport coefficients coming from the nonlinear coupling of collective modes in a liquid. In the kinetic approach to glassy behaviour, this 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 long-time limit. However, study of the equations of nonlinear fluctuating hydrodynamics [7] shows that the dynamic feedback mechanism causing a divergence of the viscosity is cut off as a result of the coupling of the density fluctuations to the current in a compressible fluid. In these so-called extended mode-coupling models [7–10] it has been shown that the dynamic transition is removed. The relaxation times keep 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 solid-like properties and it can support propagating shear waves at all length scales. In a recent work [11] the behaviour of propagating shear waves in the supercooled liquid was analysed taking into account properly

0953-8984/00/296423+08$30.00

the structural effects at high density, through a mode-coupling calculation. The extent of the slowing down in the 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 behaviour 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 there is no transition to an ideal glassy phase 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 analysing the transverse autocorrelation function. The nature of the dynamics is usually expressed in terms of the Laplace 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 Laplace-transformed form [12]

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

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 called 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 autocorrelation functions. 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 can be expressed in the form [7]

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

$\Omega_q = q/\sqrt{\beta m S(q)}$ 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:

$$\Gamma_{mc}(q,t) = \int V^L[\vec{k},\vec{k_1}]\psi(\vec{k},t)\psi(\vec{k}_1,t)\,\frac{\mathrm{d}\vec{k}}{(2\pi)^3} \tag{3}$$

where $\vec{k_1} = \vec{q} - \vec{k}$. $u = \hat{q}\cdot\hat{k}$ is the dot product of the 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 equation (2) plays a crucial role in determining the asymptotic dynamics. If γ is ignored, the simple mode-coupling approximation for the memory function provides 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 [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, ω limit, $\gamma \sim q^2$. This gave rise to a diffusive decay of the density correlation, restoring ergodicity in the long-time limit. The formal expression for the quantity γ was obtained in reference [7] using nonperturbative analysis. For the calculations here we use the one-loop results in the simplest form, in the small-q, ω limit:

$$\gamma(q, t) = \gamma_0 q^2 \int \mathrm{d}k \, [\dot{\psi}(k, t) S(k)]^2. \tag{5}$$

$\dot{\psi}$ refers to the time derivative of the function $\psi(q, t)$ and $\gamma_0 = {v_0}^2/(6n\sigma^2\pi^2)$, v_0 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 $\mathrm{O}(k_B T)$ 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 causes the dynamic correlations in the density fluctuations to be smoothed.

We solve for the time evolution of 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 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 autocorrelation 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–Weis (VW) [18] correction, this takes place at a critical value of the packing fraction $\eta^* = 0.525$ [19]. We focus our study here 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. 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, especially at short distances. In the present calculation we use for the bare transport coefficients relevant for the short-time dynamics the results obtained from hard-sphere models [20] with $\Gamma_0(x)$ and $\eta_0(x)$ 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 $x = q\sigma$, which is the wave vector q multiplied by the hard-sphere diameter σ. j_l is 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 wavenumbers, we compute the memory function in terms of the density correlation function. In the present calculation the latter is obtained from the extended MCT computation over a wide range of wave vectors, from small values up to a cut-off value. The extended mode-coupling model that is used here does produce a form of the cut-off function in the hydrodynamic limit. Indeed, for analysing 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. For small wavenumbers, as was indicated above, there is a diffusive mode restoring ergodicity. We choose the cut-off function giving a diffusive pole by approximating $\gamma(q, t)$ by the hydrodynamic limit given in (5). We assume that the cut-off function is constant [21] beyond $q\sigma = 0.015$, around

which value of $q\sigma$ the structure factor, which is the only input in the present theory, reaches within one per cent of its hydrodynamic limit. For the density range of interest here, we use this as the cut-off value for using the hydrodynamic expression for γ. To compute the transverse autocorrelation function for different wavenumbers, we use the standard form for the mode-coupling contribution to the generalized shear viscosity or the memory function:

$$\eta_{mc}(q,t) = \frac{n}{2\beta m}\int \frac{\mathrm{d}\vec{k}}{(2\pi)^3}\left[c(k) - c(\vec{k}_1)\right]^2 k^2(1-u^2)\psi(\vec{k}_1,t)\psi(\vec{k},t). \qquad (6)$$

For small q, this gives up to quartic order

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

where the vertex functions V_T are given by

$$V^{(0)} = \frac{2}{3}k^4 c'^2(k) \qquad V^{(2)} = \frac{k^2}{7}\left[4c'^2(k) + \frac{4}{3}kc'(k)c''(k) + \frac{k^2}{2}c''^2(k)\right].$$

We make detailed calculations of the transverse autocorrelation function for different values of the wavenumber and study the nature of its relaxation with time. From the study of the dynamics, a wavenumber q_0 is identified such that with $q > q_0$ the relaxation of the transverse current correlation is oscillatory, indicating that the system sustains shear waves up to this wavenumber. 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 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_0 for which the transverse autocorrelation function goes negative at a given wave vector q. We define a length $L_0 = 2\pi/q_0$ corresponding to this critical value of the wavenumber for the shear wave which corresponds to the maximum wavelength for propagating shear waves. See table 1.

Table 1. The length scale L_0 in units of σ for different values of the packing fraction η.

η	L_0
0.50	47.38
0.51	73.19
0.52	97.55
0.53	146.18
0.54	213.25
0.55	324.56
0.56	497.19
0.57	744.72
0.58	826.05
0.59	1008.36
0.60	1275.07
0.61	1457.35
0.62	3145.26

In figure 1 the transverse autocorrelation function is shown for the packing fraction $\eta = 0.57$. As the wavenumber is decreased, we see that the nature of the 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 behaviour. For $q > q_0$ the speeds of the propagating shear waves are computed from the decay of the time correlation function.

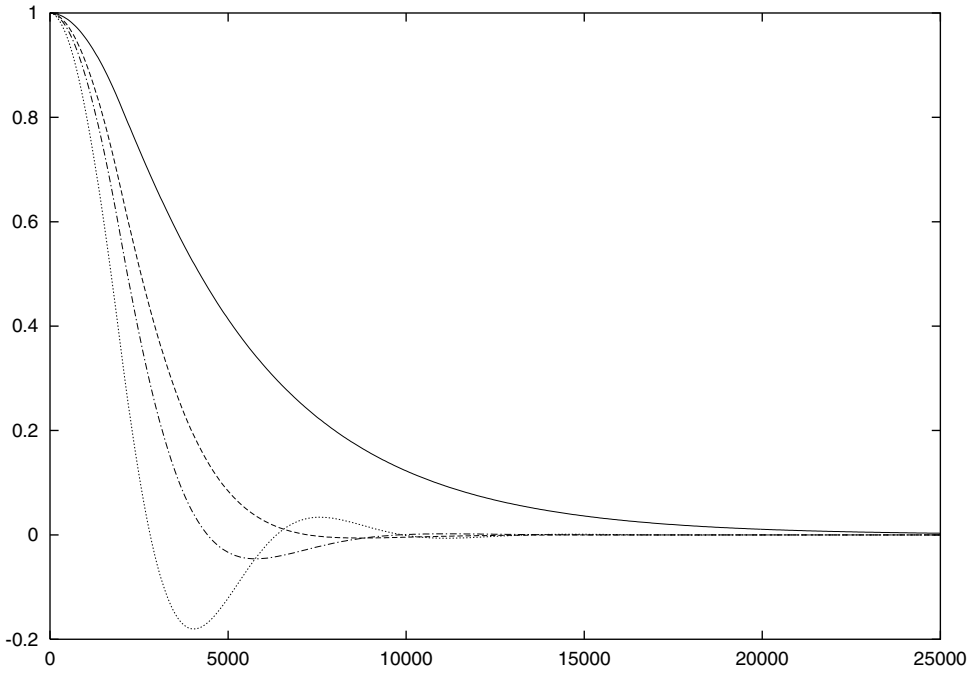

Figure 1. The normalized transverse current–current correlation function $\phi(q, t)$ for $q\sigma = 0.008$ (solid), 0.010 (dashed), 0.012 (dot–dashed), and 0.015 (dotted), at $\eta = 0.57$.

In figure 2, we show the behaviour of the speed of the shear waves versus the wave vector for the reduced density $n\sigma^3 = 1.08$. As the critical wavenumber is approached, the speed of the shear waves goes to zero. For large wavenumber the speed of the shear wave reaches its

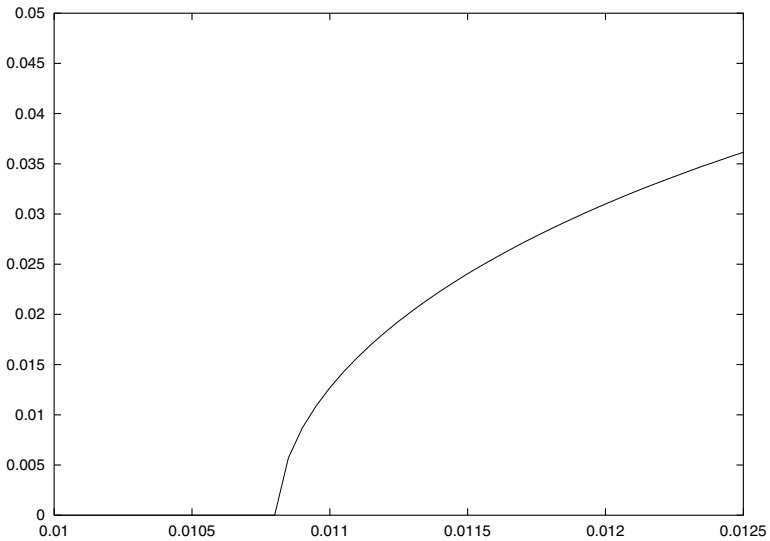

Figure 2. The speed of the shear wave in units of σ/t_E (see the text), versus $k\sigma$, at density $n\sigma^3 = 1.08$.

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_0 with packing fraction η ($=\pi n\sigma^3/6$) 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 as a less substantial enhancement takes place.

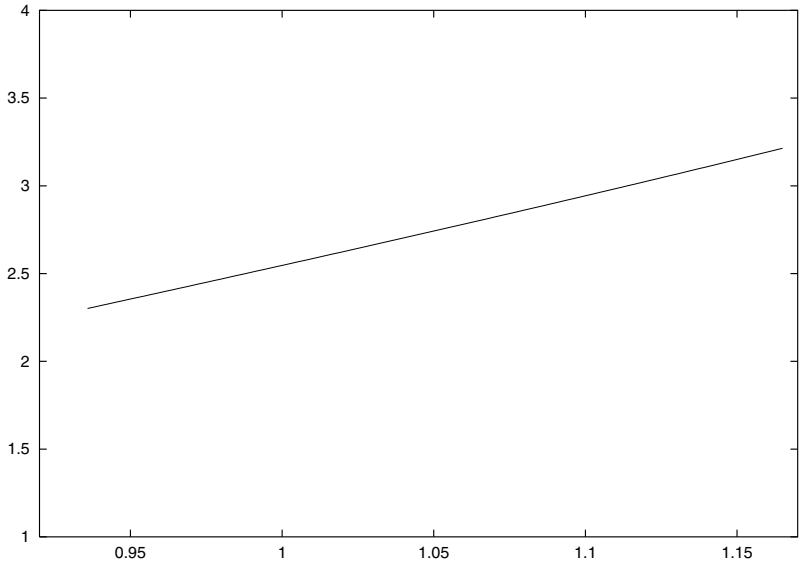

Figure 3. The shear modulus G_∞ in units of $(k_BT)/\sigma^3$ (on a $\log_{10}$ scale) versus packing fraction η.

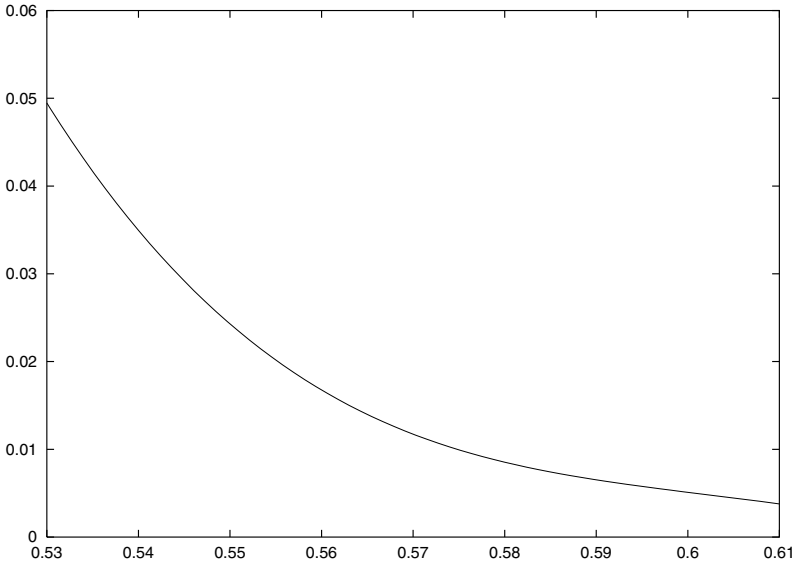

Figure 4. The wavenumber q_0 (defined in the text) in units of σ^{-1} versus the packing fraction η.

Indeed, the length scale L_0 does not represent any underlying thermodynamic phase transition, but indicates how the cooperative nature of the dynamics of the 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. Solid-like natures of undercooled liquids have also been observed from the transverse sound modes [23]. Mountain has observed [24] a similar behaviour of propagating shear waves from molecular dynamics simulations of fragile liquids, which are also systems where the mode-coupling models apply. This length scale of the 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 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 behaviour should involve the large-wave-vector extension of the mode-coupling formalism beyond the simple one-loop approximation [10] to investigate the hopping motion in the supercooled liquid. The present version of extended MCT uses the hydrodynamic form and is used to study the nature of the shear waves at small wavenumbers. It has been established by independent works [7, 9] that in the small-q limit, the final decay process restoring ergodic behaviour in the density autocorrelation 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 couplings to thermal fluctuations are also ignored in the formulation, with the assumption that the density fluctuations are the key quantity. We have also not taken into account 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]. While there can be more involved formalisms of the mode-coupling terms, the present work demonstrates that the simplest mode-coupling terms with density fluctuations are crucial to understanding shear waves. Differences even exist among the mode-coupling models for the supercooled liquid dynamics described in the literature. At the level of the ideal transition model, they are the same as regards the form of the vertex functions that appear in the theory, and thus one would expect a diverging length as described in reference [11]. However, the form of the cut-off function that is finally responsible for the absence of a sharp transition is not the same for all versions of the mode-coupling theory. The kernel used for the computation for the density correlation functions used here is obtained from the results obtained from references [7] and [9] which predicts a diffusive mode on the longest timescale. In other versions of the extended mode-coupling theory, the sharp transition is cut off through a cut-off function, though with a different wave-vector dependence. One thus expects a removal of the divergence of the length scale in those models as well. Recently, a length scale [26] was identified from a four-point time correlation function in fluids. This is also related to the solid-like nature developing at supercooled densities. Since the solid-like behaviour is finally related to the very long timescale that develops at the supercooled density, we consider that the origin of the growth on these different dynamic length scales is in the end related to that of the timescales.

In the viscoelastic theory in [27], 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. We have considered a theoretical model which is obtained from first principles. It includes as input only the static structure factor of the *liquid*. The same model has already

been used, 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 L_0 is related to the dynamic behaviour of the system and is representative of the distance over which the supercooled liquid has enough structure to sustain propagating shear waves.

Acknowledgment

The author acknowledges support under NSF project INT9615212.

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