Anomalous stretching in a simple glass-forming liquid

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The frequency dependent shear modulus $G(\omega)$ for a simple liquid shows strongly stretched behavior and the stretching exponent increases with decrease of temperature. This unconventional behavior was reported earlier in Phys. Rev. Lett. **73**, 963 (1994) from experiments on simple liquids. We demonstrate here that this is a feature of the characteristic two-step relaxation process of the self-consistent mode coupling theory of supercooled liquids.

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The extremely slow relaxation of shear in the glassy systems is one of the most important signatures of the amorphous state. Dynamic shear viscosity and the shear modulus were measured experimentally for di-*n*-butylphthalate (DBP) in Ref. [1] in the vicinity of the glass transition region. In the glassy state the relaxation behavior follows the stretched behavior slower than the Debye or exponential relaxation. In general, the relaxation gets more stretched as the temperature is lowered. However, in Ref. [1], it was reported that for the dynamic shear modulus one sees a reverse trend—namely the stretching exponent increasing with lowering of temperature. In the present paper we report a similar behavior observed for the same quantity $G(\omega)$ computed from the self-consistent mode coupling models. We show that this unconventional behavior seen in the stretching exponent is a consequence of the two-step relaxation process, which is a generic feature of the self-consistent mode coupling theory (MCT). The glassy behavior observed in supercooling the liquid has been modeled from various approaches, such as using classical statistical mechanics of many particle systems [2–4] as well as making analogy to models for spin systems [5]. The solidlike behavior of the supercooled liquid state is usually described in terms of the phenomenological viscoelastic models. A microscopic mechanism that explains viscoelasticity comes from the MCT. In the present work we compute the frequency dependent shear modulus $G(\omega)$ of the liquid from the MCT. The main input in the theory comes from the structure factor of the liquid. Our main result shows that the frequency dependence of $G(\omega)$ follows the Cole-Davidson form with an exponent β_{CD} that *decreases* with increasing temperature, similar to the anomalous behavior seen in the work of Menon *et al.*

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

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

in terms of the memory function or the generalized shear viscosity $\eta^R(q,z)=\eta_0+\eta_{mc}(q,z)$, where η_0 is the short time or bare part arising from uncorrelated motion of the fluid particles. The mode coupling contribution for η_{mc} takes into account the cooperative effects in the dense fluids. 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 function:

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

where $u=\hat{q}\cdot\hat{k}$, the dot product of two corresponding unit vectors, m is the mass of the fluid particles and $\beta=1/k_BT$. $\psi(q,t)$ is the Fourier transform of the density autocorrelation function normalized with respect to its equal time value. The direct correlation function $c(k)$ and the static structure factor $S(k)$ are related through the Ornstein-Zernike [6] relation $S(k)=[1-nc(k)]^{-1}$, where n is the equilibrium density of the liquid. For the dense fluid at small enough length scales (i.e., large enough q), the transverse current correlation decays through a damped oscillatory mode termed as the shear wave [6,7]. We focus in this work mainly on the dynamic response of the system. Here the elastic response of the supercooled liquid is defined over a time scale with the corresponding frequency dependent modulus $G(\omega)$ defined in terms of the dynamic viscosity $\eta(\omega)$ as

$$G(\omega)=\iota\omega\eta(\omega). \tag{3}$$

The high frequency limit of $G(\omega)$ denoted by G_∞ then gives the elastic response even in the normal liquid state. Following Menon *et al.* we also study a related quantity from our model, defined as [1]

$$R=\frac{\omega_p\eta(\omega=0)}{T}, \tag{4}$$

which is representative of the cooperation in the dynamics [8]. Here ω_p is the peak frequency in the imaginary part of $\eta(\omega)$. For Debye relaxation the memory function has a simple exponential decay, i.e., $e^{-t/\tau}$, where τ is the relaxation time. In this case the two quantities R and G_∞/T are identical. In our calculation, the variation of the controlling thermodynamic parameters are followed as in Ref. [9]. The critical values of these parameters, at which the transition takes place, depend on the interaction potential. In order to study the temperature dependence of the stretching we con-

sider a one-component Lennard-Jones fluid. The structure factor used in this calculation is obtained using standard methods [10] for such interaction potentials. The generalized memory function is computed from the self-consistent expression (2) in terms of the density correlation function. The latter is computed using the mode coupling theory. However, if the simple model with a dynamic transition is considered, it gives rise to an ideal glassy state with divergent viscosity at a relatively high temperature, referred to above as T_c. With the present model the dynamic transition takes place at $T_c^* = 0.912$ and $\rho^* = 0.999$. In order to consider a more realistic situation we, therefore, consider here the extended model [11] where the sharp transition is absent due to ergodicity restoring processes coming from the coupling of density and current fluctuations. For this we have used the form of the correction terms obtained [12] from the complete treatment of the nonlinearities in the hydrodynamic equations. The small wave number result [13,14] is used here for the finite wave vector range and the strength of the correction term in the theory is approximated through an over all scale δ^{-1} for the α relaxation. In the limit δ approaching zero, the ideal glass transition model is obtained [15]. In solving the MCT equations this parameter is adjusted [11] so that the viscosity of the supercooled liquid computed from the MCT agrees with the results from computer models for systems with same interaction potential. Generally, one-component Lennard-Jones (LJ) systems are difficult to be simulated in computers for study of glass transition because of the problem of supercooling due to early crystallization that occurs in such systems. However, we have made use of the recent results obtained in Ref. [9], by Angelani *et al.*, where the dynamics of one-component LJ systems were studied avoiding the crystallization process. In the formulation of the MCT used here with equilibrium correlation function, it is *assumed* that the system is supercooled below the freezing point without crystallization taking place while it is being kept very close to the equilibrium state. In the method followed in Ref. [9] crystallization is avoided by actually removing the crystal minima from the configuration space used for the master equation dynamics. In this respect the results obtained in Ref. [9] should be very suitable to be compared to MCT results. These calculations although done for a small number of particles, presented an alternative method of studying the dynamics for one-component LJ systems in the deeply supercooled state where normal molecular dynamics (MD) fails due to crystallization. The results from this master equation approach to dynamics agreed [9] with the MD simulation results in the high temperature range. We fix the cut-off parameter in the model so that the mode coupling prediction of the viscosity agrees with the corresponding result reported in Ref. [9]. We then obtain the temperature dependence of the shear modulus using the fully self-consistent solutions of the extended MCT equations. The results for the shear modulus show that the stretching exponent for the Cole-Davidson fit decreases with increase of temperature similar to the experimental observation of Ref. [1]. However, we demonstrate below that this key result reported here, i.e., the anomalous behavior in stretching, is independent of the particular form of the MCT used and *is a generic feature of the two-step relaxation process of the mode coupling models*.

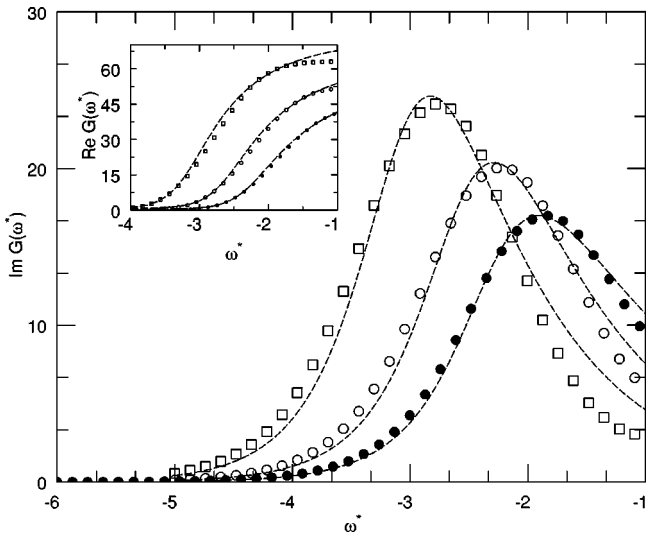

FIG. 1. Plot of imaginary part of shear modulus $G'(\omega^*)$ in units of ϵ/σ^3 vs frequency ω^* for temperatures $T^* = 0.559$ (squares), $T^* = 0.639$ (circles), and $T^* = 0.723$ (dots). Dashed lines are the corresponding Cole-Davidson fit to results from the theoretical model. Inset shows the same plots for the corresponding real parts.

We will follow the temperature variation along the line chosen in Ref. [9] with a fixed density. Next we present the results on the frequency dependent response in the supercooled liquid and its behavior with the change of temperature. The frequency dependent shear modulus $G(\omega)$ is zero wave vector limit of $G(q,\omega)$. In Fig. 1 the real and imaginary parts of the shear modulus $G(\omega) = G'(\omega) - \iota G''(\omega)$ in units of ϵ/σ^3 are plotted as a function of $\omega^* = \omega\tau$, for temperatures $T^* = 0.559$ (squares), $T^* = 0.639$ (open circles), and $T^* = 0.723$ (filled circles). Here $\tau = \sqrt{m\sigma^2/\epsilon}$ and temperature T^* is expressed in units of ϵ/k_B. The peak positions in the imaginary part of $G(\omega)$ is representative of the dominant time scale at the corresponding temperature. The frequency dependent shear modulus $G(\omega)$ is fitted to the Cole-Davidson (CD) form

$$G_{CD}(\omega) = G_\infty \left(1 - \frac{1}{(1 + i\omega\tau)^{\beta_{CD}}} \right), \tag{5}$$

where β_{CD} is the stretching exponent. The best fit to the theoretical data is shown as dashed lines in Fig. 1. In Fig. 2, we show the variation of β_{CD} (filled circles) with temperature and the corresponding experimental data of Ref. [1] in the inset. We note that the stretching exponent β_{CD} *increases* with decrease in temperature. Finally we show in Fig. 3 the quantity G_∞/T, representing the high frequency limit of the shear modulus against temperature. The theoretical calculations show that it monotonically increases with fall of temperature. This trend in the data of Menon *et al.*, which is relatively much closer to the T_g, is not so clear and seems to be more noisy. On the same plot we show the quantity R defined in Eq. (4). With the fully self-consistent evaluation of the memory function we find that both R and G_∞/T follow

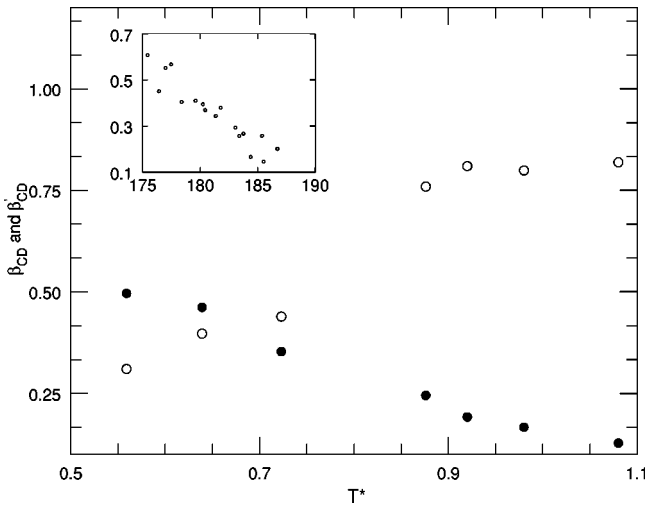

FIG. 2. Stretching exponents β_{CD} (filled circles) and β'_{CD} (see text) vs temperature T^* showing opposite trends. Inset shows the experimental data of Fig. 5 of Ref. [1].

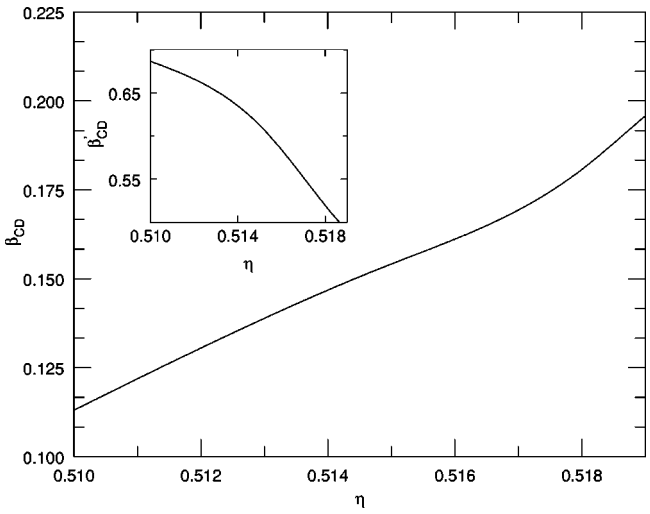

FIG. 4. Anomalous density dependence of β_{CD} for the hard sphere model. Inset shows the normal behavior in β'_{CD} (see text) with density.

the same qualitative behavior over the entire temperature range investigated here. This is also consistent with the experimental results reported in Ref. [1] for DBP. It should be noted that while the peak position w_p changes by three orders of magnitude the R changes by only a factor of 4. This is qualitatively similar to the result of Ref. [1], indicating the weak temperature dependence of R. For higher temperature regimes, R approached the value of G_∞/T as the relaxation become more Debye-like.

We have computed here the temperature dependence and the dynamic viscosity of the supercooled liquid starting from a microscopic approach where the structure of the liquid is the only input. It is obvious that in the supercooled state any model for the dynamics taking into account short time uncorrelated motions will not be very useful and the strongly correlated motions of the fluid particles are very important. The dynamical correlations of the very dense state is studied using the self-consistent MCT. In the present stage this is the only existing model for computation of shear modulus from a microscopic approach. The choice of the parameters was done to ensure that the predictions of the theory for the macroscopic viscosity agree with those from computer simulation of the model system. The calculation of $\eta_{mc}(t)$ as done in the present work, can be applied as long as the density correlation functions are obtained from any suitable method. The quantity R introduced in Eq. (4) shows qualitatively similar behavior as reported in Ref. [1] over the temperature range studied. The memory function shows the usual behavior of increased stretching with supercooling. The temperature dependence of β implies the breaking of the time-temperature superposition principle. However the stretching exponent for the shear modulus, i.e., β_{CD} *decreases* with increase of temperature, which is different from what is seen in most relaxation behaviors. This result of our theoretical model as indicated above in Fig. 2, is the key result of the paper validating the experimental observations of Menon *et al.* in the context of extended MCT. This anomalous temperature dependence of the stretching exponent is not an artifact of the choice of any particular static structure factor or other parameters in the theory. This is a result of the two-step relaxation seen in the mode coupling theory. This involves the initial power law behavior with a positive exponent changing to a stretched exponential form. The exponent of the stretched exponential relaxation part in the memory function shows a normal behavior, i.e., reduced stretching at higher temperatures. Indeed, we observe that if the relaxation function has only the stretched exponential part then, the β_{CD} for shear modulus also *shows a normal behavior*. This is shown through the primed quantities in Figs. 2 and 4 (discussed below) for two different models. However the full memory function that follows from the MCT has a two-step relaxation and with this, the anomalous behavior is observed. The wing of the power law relaxation overlaps with that of the stretched exponential form to produce the anomalous effect. It is also required that the time scales of the two processes are not widely separated. Thus we expect such a

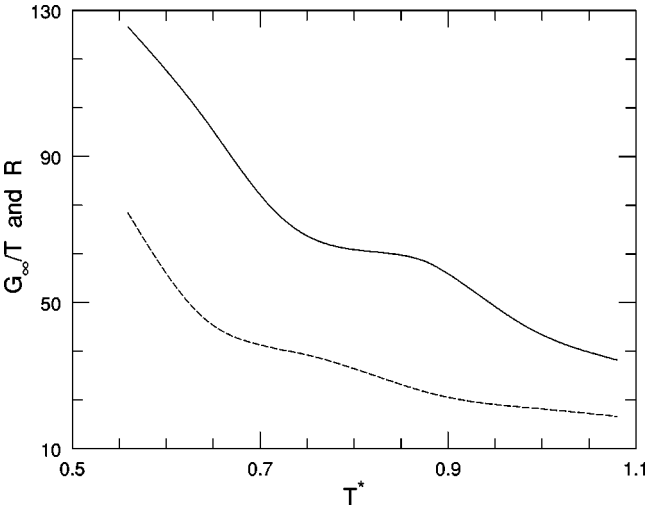

FIG. 3. Temperature dependence of G_∞/T (solid line) and $R = \omega_p \eta/T$ (dashed line).

behavior to persist over intermediate temperature ranges. We have verified this anomalous behavior of the stretching exponent β_{CD} by considering various forms of the mode coupling models. The same behavior is observed if the simple MCT model, ignoring the cut-off mechanism, is considered with LJ structure factor. For hard spheres the extended MCT can be formulated to give agreement with computer simulation results [17] and here also the same anomalous behavior results from the model. Finally, if we consider the most simple case for hard sphere systems without any cutoff, it predicts an ideal transition at packing faction $\bar{\eta}=0.525$ using Percus-Yevick structure factor with Verlet-Weiss correction [16]. In this case the stretching shows density dependence except when it is very close to the ideal transition point and here also the same anomalous behavior is observed. In Fig. 4. we show the β_{CD} obtained from the Cole-Davidson fit of the shear modulus. Here β_{CD} refers to the results obtained with the *full* memory function having the two-step relaxation and this shows the anomalous behavior, i.e., B_{CD} increases as the density increases. However, the primed quantity β'_{CD}, which is obtained from the memory function having only the stretched exponential part, shows the normal trend. The results here are established through numerical methods. However, it should also be noted that even the stretched exponential behavior in MCT is only established numerically [3,18]. The mode coupling model with the realistic structure factor as an input, provides an explanation for the viscoelastic behavior seen in supercooled liquids. The anomalous behavior seen in the stretching exponent β_{CD} is a consequence of the two-step relaxation process, which is a generic feature of all MCT models.

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