Temperature dependence of the Power law exponent of relaxation in a supercooled Liquid

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ABSTRACT

The dynamics of Lennard-Jones fluid is studied through extended mode coupling theory (MCT) with the inclusion of the slow mode of defect density. Inclusion of defect density facilitates the liquid like state for temperatures much lower than predicted from ideal MCT. From the present model the temperature dependence of the power law exponent is obtained at a constant pressure. We have also computed the wave number dependence of the power law exponent.

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Introduction

The phenomena of Glass transition has been studied extensively through theoretical \[1, 2, 3, 4, 5\] models, computer simulations \[6, 7\] as well as scattering experiments \[8, 9, 10\]. If a liquid is cooled beyond the freezing point avoiding the first order transition to an ordered crystalline state, it continues in the amorphous state with solid like properties. In this supercooled state the liquid develops very long relaxation times and the transport coefficients (viscosity) abruptly increase. A microscopic mechanism for this slow dynamics using a statistical mechanical approach has been proposed through the Mode coupling theory (MCT). This is based upon the idea \[11\] that the transport coefficients in the supercooled state gets a feedback from the nonlinear coupling of slow modes in the fluid. The effect of the structure on the dynamics is studied from the wave vector dependence of the model. MCT predicts a two step relaxation process for glassy dynamics: power law ($\beta$-relaxation) at intermediate time scales which crosses over to stretched exponential ($\alpha$-relaxation) decay of density correlation function over long time scales. In the ideal model \[12\] there is a sharp transition from ergodic to a nonergodic phase at a critical density. In the later version of more careful analysis \[13, 14, 15\] the sharp transition is finally removed from the ergodicity restoring mechanisms coming from the coupling of the density fluctuations with currents in the compressible fluid. The final ergodicity restoring mechanisms in a supercooled liquid behaves like a collective slow mode. There has been phenomenological extension of the theory to consider extra slow modes that develop in the liquid in the supercooled region. In the present work we consider an extension \[16, 17, 18, 19\] of the simple feedback mechanism of ideal MCT through the inclusion of the extra slow mode of defect density in the hydrodynamic description for the isotropic liquid. Here we use this model to study the dynamics in the simple One component Lennard-Jones fluid in the supercooled state. In this respect we like to note that previous MCT studies on LJ liquid \[20\] show that one component system freezes into a nonergodic phase at a relatively low density.
The defect density considered in the model can be associated with the vacancies in the solids or void or free volumes in the fluid. The movement of these free volumes were considered crucial for the transport in the liquid \[1\]. Following Ref. \[19\] we consider the defects to be moving in a metastable potential well. Here the extent of coupling between defect density and the particle density governs the location of the ideal glass transition point that occurs as a result of the feedback mechanism proposed in MCT. Thus at a constant pressure we observe a transition line whereas a transition point is predicted in the simple MCT. Phase diagram of coupling parameters with temperature is studied through nonergodicity parameter. We compute the relaxation dynamics of fluid in the power law regime and calculate the power law exponents. From the present model the temperature dependence of the relaxation exponents arises naturally as a consequence of the critical line. The paper is organized as follows. In next section we briefly describe the model considered followed by section III where we discuss briefly the static structure factor used in the calculation. In section IV the results for the power law relaxation as predicted by the mode coupling theory is presented. In last section a brief discussion of the work is presented.

The Model Studied

In the mode coupling theory we focus on the normalized density-density correlation function \(\psi_q(t)\). The dynamical evolution of \(\psi_q(t)\) is written in terms of an integro-differential equation,

\[
\Delta_q \ddot{\psi}_q(t) + \Gamma^0_q \dot{\psi}_q(t) + \psi_q(t) + \int_0^t ds \Gamma^{mc}_q(t-s) \dot{\psi}_q(s) = 0,
\]

where the constant \(\Delta_q = \beta m S(q)/q^2\) with \(m\) as the mass of the liquid particle and \(\beta\) is the Boltzmann factor. \(S(q)\) is the static structure factor for the liquid. The bare transport coefficient \(\Gamma^0_q\) \[21\] is defined in a dimensionless form as

\[
\Gamma^0_q = \frac{2 \Delta}{3 t_E} [1 - j_0(q^*) + 2 j_2(q^*)],
\]

\(q^*\)
where \( q^* = q\sigma \) and \( j_n(x) \) is the \( n^{th} \) order spherical Bessel function \([22]\). The Enskog time \( t_E \) \([23]\) for the LJ fluid is approximated using the equivalent hard sphere diameter. The generalized transport coefficient \( \Gamma_q(t) \) has the bare \( (\Gamma^0_q) \) as well as the mode coupling \( (\Gamma^{mc}_q(t)) \) contributions from the nonlinear coupling of density fluctuations. Following Ref. \([19]\), the mode coupling part of the generalized transport coefficient is given by,

\[
\Gamma^{mc}_q(t) = \int \frac{d\vec{k}}{(2\pi)^3} [\tilde{V}^{(1)}(q, k)\psi_k(t)\phi_{k_1}(t) + \tilde{V}^{(2)}(q, k)\psi_k(t)\psi_{k_1}(t)]
\]

with \( \vec{k}_1 = \vec{q} - \vec{k} \). Here \( \phi_{k_1}(t) \) is the normalized defect auto correlation function and gives the contribution to the transport coefficient coming from the coupling of the defect density with the density fluctuations. The mode coupling vertices with full wave vector dependence are given by

\[
\tilde{V}^{(1)}(q, k) = \frac{S(q)}{n_0} [2y\tilde{U}(q, k)S(k)S(k_1) + \kappa n_0 c(k)S(k)]
\]

and

\[
\tilde{V}^{(2)}(q, k) = \frac{S(q)}{2n_0} [\tilde{U}^2(q, k) - 2y\tilde{U}(q, k)]S(k)S(k_1)
\]

These equations are obtained \([19]\) from the nonlinear equations for the extended set of hydrodynamic variables. The vertex function \( \tilde{U} \) in \((3)\) is given by,

\[
\tilde{U}(q, k) = \frac{n_0}{q} [\hat{q}kc(k) + \hat{q}_1c(k_1)]
\]

where \( n_0 \) is the particle number density. It is assumed that the defects are moving in a metastable double well potential with \( \kappa \) and \( y \) as two dimensionless parameters characterizing the coupling of the defect densities with the particle density and the depth of the potential well. Defect density is assumed to be weakly interacting with the mass density and is treated as a variable similar to mass density. For \( \kappa = y = 0 \), \((3)\) reduces to the standard result, \([11]\). The presence of the linear term in the mode coupling vertex comes through the coupling with the very slowly varying defect correlation \([24]\). In the next section we study the implications of this feed back mechanism that arises from the coupling of the density fluctuations as well
as the defect density coupling. For this the static structure factor is taken as an input - measuring the extent of structural effects on relaxation. We use the standard model \[25\] for the Lennard-Jones Structure factor. We give a brief description of computation of the static structure factor next.

**Static Structure Factor**

In mode coupling equations interparticle interaction potential enters as an input via static structure factor \(S(q)\). For a Lennard-Jones (LJ) fluid the perturbation approach described in \[26\] is being used for the computation of the structure factor. The full Lennard-Jones potential,

\[
U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]
\]  

is divided into a repulsive part \(U_0(r)\) and an attractive part \(U_A(r)\) as,

\[
U_0(r) = \begin{cases} 
U(r) + \epsilon, & r < r_0 \\
0, & r \geq r_0
\end{cases}
\]

\[
U_A(r) = \begin{cases} 
-\epsilon, & r < r_0 \\
U(r), & r \geq r_0
\end{cases}
\]

with \(r_0 = 2^{1/6}\sigma\). A trial system with hard sphere diameter \(d \leq r_0\) and an attractive potential energy part \(U_A(r)\) is taken. One then finds the appropriate diameter \(d\) through perturbation approach until \(e^{\beta U_T(r)}g_T(r) = e^{\beta U(r)}g(r)\). Where, subscript \(T\) represents the trial system. Once the hard sphere diameter \(d\) is known the static structure factor for the LJ liquid is approximated by,

\[
S(q) = S_T(q) + \rho \int dr[e^{\beta U_T(r)}g_T(r)]e^{-\beta U(r)} - e^{-\beta U_T(r)}]e^{-iqr},
\]  

For the trial hard sphere system the Percus-Yevick \[23\] solution with Verlet-Wiess correction \[27\] is used.
Power law exponents

The ideal transition from an ergodic phase (fluid) to a non-ergodic (glass) phase is characterized in terms of non-ergodicity parameter defined as, \( \psi_q(t \to \infty) = f(q) \). In the long time limit or \( z \to 0 \) limit of the Laplace-transformed form of the equation (1) reduces to

\[
\frac{f(q)}{1 - f(q)} = \int \frac{d^3k}{(2\pi)^3}[V^{(1)}(q,k)f(k) + V^{(2)}(q,k)f(k)f(k_1)]
\]

(9)

where vertices \( V^{(1)} \) and \( V^{(2)} \) are given by equation (4) and equation (5). These set of coupled equations are solved self-consistently for \( f(q) \). In solving the integral equations a maximum cutoff for the wave vector integration \( \Lambda \sigma = 30.0 \) with 200 grid points is used. A set of critical parameters \( (\kappa_c, y_c, \rho_c, T_c) \) are identified below which all \( f(q)'s \) converge to zero values (ergodic phase) and above that critical point all \( f(q)'s \) converge to nonzero values (nonergodic phase). The critical points \( (y_c, \kappa_c, \rho_c, T_c) \) in \( T - \kappa \) phase space are located by fixing \( y_c = 0.15 \) and varying \( \kappa \) and \( T \). Here we study the equations with the thermodynamic parameters changing in a way so that the volume change with the temperature keeping the Pressure constant, \( P^* = P\sigma^3/\epsilon = 0.5 \) as shown in Fig. 1. Then, at a fixed pressure, we observe a line of transition giving different critical temperatures with different values of the metastability parameters. In the ideal model under similar conditions a single transition point is obtained. Along this transition line at a fixed pressure we calculate, from the solutions of the MCT equations, the power law exponent for relaxation in the LJ fluid as a function of temperature and density. We study the relaxation over time scales longer than the microscopic time scales \( t > (\Omega_q \tau)^{-1} \), where \( \tau \) is the Lennard-Jones time \( (m\sigma^2/\epsilon)^{\frac{1}{2}} \), but shorter compared to the \( \alpha \)-relaxation time scales. The dynamical equation (1), for density correlation function \( \psi_q(t) \) is solved self consistently along the transition line shown in Fig. 1. The metastable potential well for defects used for computing vertex functions is shown in Fig. 2 at critical parameters \( (T_c = 0.544, y_c = 0.15, \kappa_c = -0.038) \). The observed relaxation
behavior is given by,

$$\psi_q(t) = f_c(q) + C h(q)(t/t_o)^{-\alpha}$$  \hspace{1cm} (10)$$

where C is a constant and $t_o$ is the time scale over which the power law relaxation persists. In Fig. 3 we show the decay of density correlation function with time ($t/\tau$). The fit to the power law exponent is shown by dotted lines and the solid line represents the result from MCT equations for temperature $T_c = 0.544$ in the power law regime. Temperature dependence of the power law exponent $a$ is studied at a constant pressure $P^* = 0.5$. The exponent $a$ is calculated at the transition temperatures for fixed $y_c = 0.15$ and the corresponding $\kappa'_c's$. Fig. 4 shows the variation of the power law exponent $a$ with temperature. We also calculate the wave vector dependence of the power law exponent $a$. Fig. 5 shows the exponent $a$ along the wave vector $q\sigma$ at $T = 0.544$ and $\rho = 0.958$. In the inset the static structure factor is shown to depict the alignment of the maxima of $S(q\sigma)$ with minima of exponent $a$ and vice-versa. The arrows are shown at the maxima and minima. The power law exponent is minimum at the peak of the static structure factor, which reflects the characteristic slow relaxation at the diffraction maximum for liquids.

**Discussion**

In the simple mode coupling theory there is a single transition point with a fixed $T_c$. As a result of which the power law exponent determined in its vicinity is temperature independent. In the present case through the coupling of the density fluctuations with defect motions a line of dynamic instability is predicted and this results in a temperature dependent exponent. Here we consider the simple one component LJ system and we obtain an oscillatory behavior of the power law exponent $a$ - as shown in Fig. 4. For hard sphere system a similar oscillatory behavior is found [28] from the solutions of the MCT equations. This was also shown to agree with the power law exponent that was calculated from fitting of the light scattering data on Colloids[11]. A similar behavior was observed in the wave vector dependence of the
exponent as well. Computer simulations of one component systems at metastable densities are particularly rare due to problem of crystallization and at this time we are unable to find simulation data to look for such behavior. However simulation results for binary mixtures exist and we studied the data reported in ref. [29] without restricting to a fixed non-ergodicity parameter (NEP) as in the ideal model that gives rise to a single exponent. We do observe in this case a qualitatively same oscillatory behavior for the exponent $\alpha$ of the simulation data as shown in Figure 6. The NEP that is obtained in our fitting also shows qualitatively similar behavior as predicted from the extended model studied here. The present model can be extended to the $\alpha$-relaxation regime as well where the combined role of the density fluctuation and the defect fluctuation need to be considered.

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Figure Captions

Fig 1: Phase diagram in $T-\kappa$ space at $y_c = 0.15$ along a constant pressure line. Temperature is expressed in units of $\epsilon/k_B$.

Fig 2: Variation of depth of the potential with $n/n^*$ for $T^*_c = 0.544$. In the figure $h^*(n)$ represent the dimensionless quantity $h(n)\beta\epsilon n\sigma^3$.

Fig 3: Decay of normalized density-density correlation function $\psi_q(t/\tau)$ with time $(t/\tau)$ at
\[ T = 0.544. \] Where \( \tau \) is the Lennard-Jones time \( (m\sigma^2/\epsilon)^{\frac{1}{2}} \). Dotted lines show the power law fit (10) (see text).

Fig 4 Variation of power law exponent \( a \) as a function of temperature \( T \). \( T \) is expressed in units of \( \epsilon/k_B \).

Fig 5 : Variation of exponent \( a \) as a function of wave number \( q\sigma \) for a packing fraction \( T = 0.544 \). In inset static structure factor is shown along wave number \( q\sigma \).

Fig 6 : Variation of power law exponent \( a \) with temperature as obtained by fitting 10(see text) to the self correlation function data from Ref. [29] at wave vector \( q = 7.22 \).
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glass

liquid
\[ \psi_q(t/\tau) \]
