PHYSICAL REVIEW E **72**, 031509 (2005)

Bridging the gap between the mode coupling and the random first order transition theories of structural relaxation in liquids

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(Received 25 April 2005; revised manuscript received 5 July 2005; published 30 September 2005)

A unified treatment of structural relaxation in a deeply supercooled glassy liquid is developed which extends the existing mode coupling theory (MCT) by incorporating, in a self-consistent way, the effects of activated events by using the concepts from the random first order transition (RFOT) theory. We show how the decay of the dynamic structure factor is modified by localized activated hopping events called instantons. The instanton vertex added to the usual MCT depicts the probability and consequences of such an event. In the vertex, the probability is proportional to $\exp(-A/s_c)$ where s_c is the configurational entropy. Close to the glass transition temperature, T_g, since s_c is diminishing, the activated process slows beyond the time window and this eventually leads to an arrest of the structural relaxation as expected for glasses. The combined treatment describes the dynamic structure factor, $\phi(t)$, in deeply supercooled liquid fairly well. We show that below the mode coupling transition temperature, T_c, $\phi(t)$ not only decays via the hopping channel but the otherwise frozen MCT part of $\phi(t)$ also shows a hopping induced decay. This decay is primarily due to the relaxation of the longitudinal viscosity which is otherwise divergent in the idealized MCT. We further show that although hopping motion induces a decay in the MCT part of $\phi(t)$, due to the self-consistent calculation, this effect is nonlinear in nature.

DOI: 10.1103/PhysRevE.72.031509 PACS number(s): 64.70.Pf

I. INTRODUCTION

Inelastic neutron scattering has given detailed structural information on how transport in liquids changes as they are cooled in the glassy state [1,2]. Many of the structural details are well described by mode coupling theory (MCT) but that approach does not describe well the dynamics of the deeply supercooled state [3–9]. The random first order transition (RFOT) theory of glass explains this lacuna of MCT [10–12]. In this paper we show how RFOT theory can bridge the gap between the onset of glassy dynamics at high temperatures and the low temperature behavior and thus provide a unified view of the structural dynamics in a deeply supercooled region. Over the last few decades, experimental and theoretical studies on the phenomenological aspects of the glass transition have been the subject of a vast scientific literature. A glass forming liquid is characterized by its ability to circumvent crystallization on rapid cooling to a temperature well below its freezing temperature T_m. In contrast to crystal formation what is most remarkable about solidification into an amorphous state is that the structure changes accompanying vitrification are either very small or unobservable. However, on passage through supercooled regime the dynamic and thermodynamic behavior of the liquid exhibits a number of anomalies as it eventually transforms to an amorphous solid, called a glass.

The density-density correlation function at finite wave vector probed by neutron scattering, $\phi_k(t)$ for a system approaching glass transition first decays via a fast microscopic process which is followed by a plateau in the intermediate time. The dynamics while approaching the plateau is nonexponential, power law in nature and is called the β relaxation. The time scale of the β relaxation is predicted to show a power law divergence. The decay from the plateau known as the initial α relaxation is also given by a power law, known as von Schweidler law. The exponents in the β and the initial α relaxation regimes are different in value but related to each other. The slow α relaxation which appears in the long time is described by a stretched exponential or Kohlrausch-Williams-Watts (KWW) function [2].

The thermodynamic and kinetic anomalies at T_g are known experimentally to be correlated. One experimentally finds a sharp rise in the measured heat capacity of a liquid during heating which follows prior to cooling a constant rate [13], the cycle being well extended on either side of the glass transition region. The over shoot of the heat capacity is taken to be a thermodynamic signature of a glass to liquid transition. However, what lies at the heart of glass transition is the dramatic slowing down of molecular motion that occurs progressively on cooling after the plateau in the inelastic structure factor appears. This is manifested by a phenomenal increase in shear viscosity η (also the characteristic structural relaxation time τ) by several orders of magnitude for a relatively modest decrease of temperature (by few tens of degrees). The glass transition seen in the laboratory is in fact best described as a kinetic phenomenon which marks the falling out of the equilibrium due to the inability of molecular rearrangement within the experimental time scale as temperature T is lowered. A conventional definition of the transition temperature T_g is the temperature at which the viscosity, η reaches a value $10^{13}P$.

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The mode coupling theory makes detailed predictions of the temperature dependence of the time evolution of the density-density correlation function [3]. The emergence of a plateau in the neutron scattering is one of the important predictions of the ideal mode coupling theory. At a quantitative level both the emergence of a plateau in the dynamic structure factor at high temperature and the exponential slowing of the dynamics at low temperature are also explained by the random first order transition (RFOT) theory [10,11]. Idealized MCT can also correctly predict the power law dynamics in the β and the initial α relaxation regimes and the relation between the exponents in these two regimes. It can also predict the stretched exponential in the late α relaxation regime. However, MCT strictly applied predicts a premature arrest of the decay of the density-density correlation function. The dynamical plateau of MCT was contemporaneously obtained by a variety of static approaches based on self-consistent phonon calculations and density functional theory which forms the origin of the RFOT theory [14,15]. MCT would appear to predict a dynamic arrest of the liquid structural relaxation, arising solely from a nonlinear feedback mechanism on the memory function. This feedback mechanism was first proposed by Geszti [16] to describe the growth of viscosity in a previtrification region and involves a self-consistent calculation of the dynamical correlation function and transport coefficients. In RFOT theory one sees the dynamic arrest is connected with the emergence of a mean field free energy landscape.

According to the MCT, the essential driving force for glass transition is the slowing down of the density fluctuations near the wave number, $q \simeq q_m$ where the static structure factor is sharply peaked. Thus, the glass transition does not appear to be caused by any small wave number (infrared) singularity present in the static structure factor, but rather it is a phenomenon where the intermediate wave numbers are important. Near the dynamical transition there is a general slowing down of all the dynamical quantities, and due to the softening of the heat mode near $q=q_m$, this slowing down is most effectively coupled to wave numbers near q_m. The glass transition temperature predicted by MCT, T_c, always exceeds the laboratory T_g. The explanation for this was pointed out by Kirkpatrick and Wolynes [17]. Since there are exponentially many aperiodic structures any single one of them is unstable to transform to the other. At T_c the system is not frozen because activated events allow interconnection between these structures. Thus T_c can be identified as a crossover temperature below which activated motions occur in which groups of particles move in a cooperative way over local barriers in the free energy landscape. Computer simulation studies have amply demonstrated this change of transport mechanism and have explicitly revealed the presence of such hopping motions in deeply supercooled liquids when the usual convective diffusive motions cease to exist [18,19]. Simulations also show that these hopping events relax the local stress in the system [20].

These properties of the activated events below T_c can be represented by the random first order transition theory in a way superficially analogous to the theory of nucleation at random first order transition (although there are some differences). Calculation of fluctuations and transport in deeply supercooled or glassy medium are most easily made where the reference is an ideal glassy state and where the configurational entropy has vanished [10,21,22]. The barriers for activated dynamics vanish as the temperature of the system approaches the dynamical transition temperature from below, much like that at a spinodal. The barrier for activated events can be described as a nucleation phenomenon where the free energy change is a sum of the entropy change due to the formation of an entropy droplet and a surface term with a radius dependent surface energy [10,11]. A more explicit view of the similarities and the differences from nucleation appears in the recent work of Lubchenko and Wolynes and the elegant analysis of Bouchaud and Biroli [23]. Deep in the supercooled regime, the nucleation free energy barrier is given by the following simple expression:

$$\Delta F^{\star}/k_B T = 32 k_B / s_c, \tag{1}$$

where s_c is the configuration entropy of a single moving bead, i.e., an equivalent spherical particle. The coefficient 32 arises from a specific microscopic calculation and reflects the entropy cost of localizing a particle to vibrate in the cage, explicitly observed in the plateau of the dynamic structure factor. If one approximates s_c near the Kauzmann temperature T_K by $s_c = \Delta c_P (T - T_K)/T_K$, one then obtains the empirical Vogel-Fulcher-Tammann (VFT) law, with a relation between the liquid's fragility and the heat capacity jump, Δc_P. This expression agrees well with experimental results. However, Eq. (1) is an asymptotic form of the barrier, valid only near T_K and as will be discussed later, if we take into account the barrier softening effect near T_c then the value of the barrier will be considerably smaller than that given by Eq. (1) [11]. This effect is found to be stronger as we move away from T_K. Once the estimation of the barrier height is made the relaxation time τ is calculated, using $\tau/\tau_0 = \exp(\Delta F^{*}/k_B T)$. The random first order phase transition theory also provides an explanation of the dominant source of nonexponentiality in relaxation dynamics in terms of distribution of the configuration entropy of the activated droplet. If one assumes a Gaussian distribution of the barrier, then the standard deviation of the barrier height at T_g also turns out to be related to the specific heat discontinuity of the supercooled liquid. This correlation between nonexponentiality and ΔC_p is observed in the laboratory [24].

In this paper we use the concepts of mode coupling theory and random first order transition theory to include both the convective diffusional motion (given by MCT) and the hopping motion (described by RFOT) in the dynamics. It should be mentioned that the ergodicity restoring hopping was first introduced by Das and Mazenko [25] in their fluctuating nonlinear hydrodynamic theory and later by Gotze and Sjogren [6,8] in their extended MCT. Both the approaches are microscopic in nature where in the memory kernel of the structure factor, not only the coupling to density but also to the current modes (higher order MCT terms) are included. The coupling to the longitudinal current mode modifies the memory kernel and gives rise to an additional decay channel. This extra decay channel was found to be most effective below T_c and led to the decay of the dynamic structure factor in the long time. Thus both the theories succeeded to eliminate the ergodic to nonergodic transition at T_c. However, this extra term which gives rise to the decay is extremely complicated in nature and its connection to the activated event is not immediately apparent. The above-mentioned attempts demonstrate that it might be extremely difficult to microscopically incorporate the hopping dynamics in MCT. Thus our approach here is partly phenomenological in nature although we incorporate all the self-consistencies required by MCT.

Here we first discuss the effect of hopping alone on the structural density fluctuations. The rate of hopping and the size of the region involved in hopping are calculated from RFOT theory [11]. It is shown that hopping opens up a new channel for the structural relaxation. Next we present the equation of motion for the density-density correlation function where we take a more phenomenological approach and consider the diffusional and the hopping motions as two parallel channels for the structural relaxation in the liquid. In the same spirit as in the case of the idealized MCT the equation of motion which now has hopping motion in it is calculated self-consistently with the longitudinal viscosity. We find that in this self-consistent calculation there is a hopping induced lowering of the zero frequency longitudinal viscosity value which leads to a continuous diffusive motion even below T_c. The feedback mechanism which gave rise to the divergence of the viscosity in the idealized MCT [4] is also present in our theory but due to the presence of hopping, the divergence is shifted to a lower temperature where the RFOT hopping rate now finally vanishes only as the configurational entropy goes to zero.

II. THEORETICAL SCHEME

We propose a unified structural description covering the whole temperature regime, from the high temperature microscopic dynamics described by collisional physics to the low temperature collective many particle activated dynamics. The mode coupling theory analyzes liquid state dynamics by starting from a gaslike mode of transport but including correlated collisions and back flow. MCT does a good job describing structural correlations observed by neutron scattering in the normal liquid regime. MCT can also describe the dynamics approaching the supercooled regime but fails below T_C, where activated processes also contribute substantially. A deeply supercooled liquid explores a very rugged underlying free energy surface. The dynamics within each well may still be described by the idealized MCT which does not take into account the possibility of hopping between wells. Activated events represent essential singularities in the noise strength and thus are not contained in the perturbative MCT. To include the effect of activated events on dynamical structure factor, we need to calculate two different quantities. First, we need to calculate the effect such an event (which we call "popping up of an instanton") would have on the dynamic structure factor. The impact of such an instanton depends both on its size, that is, how many molecules are involved in the activated event and on how far particles are displaced by an activated transition. In RFOT theory, these quantities are the dynamical correlation length ξ and the Lindemann length d_L. Second, we need to estimate the probability of such an activated event occurring. We can estimate both the probability and the other quantities from the random first order transition theory using thermodynamic and structural information alone. Since these activated events affect the diffusive dynamics (described by MCT) and vice versa they cannot be treated independently but need to be calculated in a self-consistent manner. For this self-consistent treatment we adopt two different approaches and show that both the approaches provide similar results.

A similar underlying physical picture to that presented here has been put forward by Fuchizaki and Kawasaki [26] using what they called dynamic density functional theory (DDFT) to go beyond the MCT. In this coarse-grained description one considers the time evolution of the density field on a lattice. The dynamics is supposed to be given by a master equation and the free energy functional is taken from Ramakrishna-Yussouff (RY) theory [27]. As shown by Singh, Stoessel, and Wolynes [15], RY theory can produce multiple minima. Fuchizaki and Kawasaki have shown that transitions between such minima allow the structural relaxation of the coarse grained density field. They show these transitions give rise to a stretched exponential relaxation. In their calculation, the overlap between the time dependent density field and the reference one of the same lattice site takes a constant value, close to unity, in the liquid but in the supercooled state, the overlap is less than one and decreases via discrete jumps which they have connected to activated hopping transition over free-energy barriers. They have further defined an order parameter which is the overlap of the density fields at different lattice sites. The distribution of the order parameter in the normal liquid regime is sharply peaked around unity but at higher density the distribution is broad and peaked around a value less than unity. The broad distribution reflects the multiminima aspects of the free-energy landscape.

However, due to the temporal coarse graining the initial decay of the dynamic structure factor, $\phi(t)$, and the subsequent plateau are missed in their analysis. The present unified theoretical treatment provides a $\phi(t)$ which produces a correct behavior over the full time and temperature plane, and also provides an analytical expression of the dynamic structure factor where hopping alone is considered from a microscopic point of view and is connected to the entropy crisis via the RFOT theory. It is worth re-emphasizing that as a consequence of our self-consistent calculation hopping renormalizes the dynamics described by MCT.

III. EFFECT OF HOPPING ON DENSITY RELAXATION

Here we describe the hopping in terms of the popping up of a single instanton which is an activated event whose probability is obtained from the random first order transition theory. Let us say that an instanton pops up at a position R. We will take this region of influence to be spherical on the average. Good arguments suggest the region actually is fractal or stringlike [28]. But the effect will ultimately be spherically averaged anyway as we shall see below. The particles within the sphere of radius ξ around the position R will be displaced by a Lindemann length, d_l. Now the change in density $\rho(r)$ due to a single instanton popping up can be written as

$$\delta\rho^{\text{new}}(\mathbf{r},t+\delta t) = \delta\rho(\mathbf{r},t) + \theta((r-R)<\xi) \times \left(\int dt' \int_{\mathcal{D}(R)} d\mathbf{r}'\, \delta\rho(\mathbf{r}',t') G(\mathbf{r},\mathbf{r}',t-t') \times \theta((r'-R)<\xi) - \delta\rho(\mathbf{r},t) \right), \tag{2}$$

where $\theta((\mathbf{r}-\mathbf{R})<\xi)$ provides the effect of the instanton felt at the position $\mathbf{r}$, provided it is within the radius ξ. $G(\mathbf{r},\mathbf{r}'t-t')$ is the Greens function which determines the effect of instanton in moving particles from position $\mathbf{r}$ to a new one $\mathbf{r}'$, typically Lindemann length away during time t and $t+\delta t$. $\mathcal{D}(R)$ determines the region where the effect of the instanton is felt.

Since a given instanton pops up at a specific location the transformation is not translationally invariant, but when averaged over the droplet location and orientation we restore translational and rotational invariance,

$$\begin{aligned}\overline{\delta\rho}^{\text{new}}(\mathbf{r},t+\delta t) &= \delta\rho(\mathbf{r},t) + \frac{1}{V}\int d\mathbf{R}\,\theta((\mathbf{r}-\mathbf{R})<\xi) \times \\ &\quad \times\left(\int dt' \int_{\mathcal{D}(R)} d\mathbf{r}'\, \delta\rho(\mathbf{r}',t') \right. \\ &\quad \left. \times G(\mathbf{r},\mathbf{r}',t-t')\,\theta((\mathbf{r}'-\mathbf{R})<\xi) - \delta\rho(\mathbf{r},t) \right) \\ &= \delta\rho(\mathbf{r},t) + \frac{1}{V}\int dt' \int_{\mathcal{D}(R)} d\mathbf{r}'\, \delta\rho(\mathbf{r}',t') \\ &\quad \times G(\mathbf{r},\mathbf{r}',t-t')\,\Omega(\mathbf{r}'-\mathbf{r}) - \frac{v_0}{V}\delta\rho(\mathbf{r},t),\end{aligned} \tag{3}$$

where

$$\begin{aligned}\Omega(\mathbf{r}-\mathbf{r}') &= \int d\mathbf{R}\,\theta((\mathbf{r}-\mathbf{R})<\xi)\,\theta((\mathbf{r}'-\mathbf{R})<\xi) \\ &= \frac{1}{12}\pi(4\xi+|\mathbf{r}-\mathbf{r}'|)(2\xi-|\mathbf{r}-\mathbf{r}'|)^2 \\ &\quad \text{for } (\mathbf{r}-\mathbf{r}') \leqslant 2\xi \\ &= 0 \quad \text{for } (\mathbf{r}-\mathbf{r}') > 2\xi\end{aligned} \tag{4}$$

is the overlap volume of two spheres of radius ξ centered at r and r', respectively, and

$$v_0 = \int d\mathbf{R}\,\theta((\mathbf{r}-\mathbf{R})<\xi) = \frac{4}{3}\pi\xi^3 \tag{5}$$

is the volume of the region participating in hopping. ξ defines the region of hopping which is calculated from RFOT theory [11].

According to the RFOT theory, ξ is of the order of a molecular length, a at T_c but diverges as $(T-T_K)^{-2/3}$ as the Kauzmann temperature is approached. Near T_g (where the time scale is of the order of 1 hour) ξ is universally ~5 molecular lengths [11].

Thus expanding $\overline{\delta\rho}^{\text{new}}(\mathbf{r},t+\delta t)$ about t we get

$$\frac{d\overline{\delta\rho}^{\text{new}}(\mathbf{r},t)}{dt}\delta t = \frac{1}{V}\left(\int dt' \int_{\mathcal{D}(R)} d\mathbf{r}'\, \delta\rho(\mathbf{r}',t') G(\mathbf{r},\mathbf{r}',t-t')\,\Omega(\mathbf{r}'-\mathbf{r}) - v_0\delta\rho(\mathbf{r},t) \right). \tag{6}$$

Now let us say that the rate of a particle hopping is given by p_h. Thus the probability of any particle hopping in the region of volume V during the time interval δt is $p_h V \times \delta t / v_p$, where v_p is the volume of a particle (a particle will be a bead according to RFOT theory). If we include this information in the above equation and take a Laplace transform we get

$$s\overline{\delta\rho^{\text{new}}(\mathbf{q},s)} - \overline{\delta\rho^{\text{new}}(\mathbf{q},t=0)} = \frac{p_h}{v_p}\left(\int d\mathbf{q}_1 G(\mathbf{q}_1,s)\Omega(\mathbf{q}-\mathbf{q}_1)\delta\rho(\mathbf{q},s) - v_0\delta\rho(\mathbf{q},s) \right). \tag{7}$$

Thus we obtain

$$\phi_{\text{hop}}(q,s) = \frac{\phi_{\text{hop}}(q,0)}{s+(v_0-\widehat{\Omega G}(q,s))p_h/v_p}, \tag{8}$$

where

$$\widehat{\Omega G}(q,s) = \int d\mathbf{q}_1 G(\mathbf{q}_1,s)\Omega(\mathbf{q}-\mathbf{q}_1). \tag{9}$$

In the above theory the length scale of the Greens function is given by the Lindemann length d_l where as the length scale of Ω is given by ξ. Since $\xi \gg d_l, G(q,s)$ has a much slower decay with q than $\Omega(q-q_1)$ which implies that the product decays slowly with q. The propagator $G(q,s)$ should be just the short time part of the self-dynamic structure factor.

The random first order transition theory gives us the estimate of ξ, that is the spatial extent of the instanton and also the rate at which the instantons pop up that is p_h, or more properly its distribution. According to RFOT theory the fluctuations of entropic driving force leads to a distribution of hopping rates p_h [12]. This should be related to the waiting time distribution of hopping, as discussed by DeMichele and Leporini [29]. To account for this we can consider that there are n-type of instanton with lifetimes (τ_j) and with occurrence probability p_h^i. In this case Eq. (8) can be averaged over different instanton lifetimes and rates. Here, for simplification we replace p_h by the average hopping rate P which is given by $P=(1/n)\Sigma_i p_h^i$. Since hopping rate is small (that is, hops are rare), we can assume that the duration or lifetime of a hop (instanton popping up) is infinitesimally small.

Now we can write

$$\phi_{\mathrm{hop}}(q,s) = \frac{1}{s + (v_0 - \Omega \hat{G}(q,s))P/v_p} = \frac{1}{s + K_{\mathrm{hop}}(q,s)}. \tag{10}$$

As mentioned earlier, the length scale of the Greens function is determined by the Lindemann length d_l. If we neglect its frequency dependence then the Greens function can be written as

$$G(q) = \frac{1}{(2\pi)^{3/2}} e^{(-q^2 d_l^2)}. \tag{11}$$

With the above-mentioned frequency independent Greens function the expression for K_{hop} also becomes independent of frequency and only depends on the wave number. The wave number dependent hopping kernel, K_{hop} can be written as

$$K_{\mathrm{hop}}(q) = \frac{P}{v_p}\left[v_0 - 8\int_{\pi/\xi}^{\infty} dq_1 q_1^2 e^{-q_1^2 d_l^2} \times \left(\frac{[-(q-q_1)\xi \cos((q-q_1)\xi) + \sin((q-q_1)\xi)]^2}{(q-q_1)^6} \right) \right]. \tag{12}$$

We would need this expression to calculate K_{hop} in Sec. V B.

Calculation of the hopping rate from RFOT theory: We briefly discuss the calculation of the hopping rate P from the RFOT theory. As has been discussed before, the hopping rate of an instanton is connected to the free energy barrier, which in turn is connected to the configurational entropy of the system [10,11] and an asymptotic form of that is given by Eq. (1). Note that, in glasses, we need the interface energy between two alternative amorphous packings and not between two thermodynamic phases, like a solid and a delocalized uniform liquid. The alternative phases in glass become more alike at T_c. The interfacial energy (surface tension) that enters in the calculation of the instanton barrier is smaller at T_c than at lower temperature. This effect has been discussed by Lubchenko and Wolynes who termed it as barrier softening. A rigorous estimate of the barrier requires complex replica instanton calculations as recently outlined by Franz [30] and by Dzero, Schmalian, and Wolynes [31]. An alternative method motivated by variational reasoning proposed by Lubchenko and Wolynes is to write a simple interpolation formula for the free energy which allows the system to choose the smallest available barrier, and is given by [11]

$$\Delta F(r) = \frac{\Gamma_K \Gamma_A}{\Gamma_K + \Gamma_A} - \frac{4\pi}{3} r^3 T s_c, \tag{13}$$

where Γ_K and Γ_A are the surface energy terms at T_K and T_A, respectively. T_A gives a mean field estimate of temperature at which a soft crossover to the onset of activated transport takes place or the temperature at which the barrier disappears when approached from below. The expression for the surface energy at T_K is $\Gamma_K = 4\pi\sigma_o a^2 (r/a)^{3/2}$, where $\sigma_o = \frac{3}{4}(k_B T/a^2)\ln((a/d_L)^2/\pi e)$ is the surface tension coefficient and a is the molecular bead size which refers to the size of the quasispherical parts of any aspherical molecule. The bead count b for each molecule is also calculated within RFOT theory. The expression for the surface energy at T_A is $\Gamma_A = 4\pi \Delta f a^3 (r/a)^2$, where

$$\frac{\Delta f}{T_A s_c^A} = 4\left(\frac{t}{t_K}\right)^{3/2} (1/\sqrt{1 + 3t/t_K}),$$

where $t = (1 - T/T_A)$ and Δf, the excess free energy density computed from the density functional. Note that Eq. (13) tends to Γ_K as $T \rightarrow T_K$ and similarly, to Γ_A as $T \rightarrow T_A$. From the above expression of the barrier, the critical barrier free energy, $F^*(r)$, can be calculated as the maximum value of $F(r)$. Microscopic calculation giving T_A can then be used with Eq. (13) to calculate the value of viscosity, $\eta/\eta_0 = \exp(\Delta F^\star / k_B T)$ (where η_0 is the viscosity at the melting temperature, T_m and is obtained from experiments). Rather than carrying out complete microscopic calculations, Lubchenko and Wolynes used this approach to fit the experimental values of viscosity, where the values of the transition temperature T_A and $s_{\mathrm{fit}}[s_c = s_{\mathrm{fit}}(1 - T_K/T)]$ are used as the fitting parameters. T_K is obtained from thermodynamics. For example, T_K is known to be 175 K for Salol.

For our calculation of the hopping rate P, we use Eq. (13) with the fitted values of T_A and s_{fit} from Lubchenko and Wolynes [11]. Thus $P = (1/\tau_0)\exp(-\Delta F^\star / k_B T)$, where τ_0 is the time scale of the system at the melting point T_m which is taken from the experimentally known value [32]. The above expression would predict that rate of hopping becomes of the order of hours at $T = T_g$ and vanishes at $T = T_K$ [11].

We also need an estimate of the size of the hopping region ξ which has a temperature dependence and is equated to the r value where in Eq. (13), $F(r) = 0$.

IV. THE TOTAL DENSITY-DENSITY TIME CORRELATION FUNCTION

In the preceding section we have evaluated the change in the dynamic structure factor due to hopping alone. In this section we incorporate this effect along with mode coupling feedback terms in the full density-density correlation function in a self-consistent manner. The MCT part of the dynamics has been adopted from Leutheusser's work [4]. We are aware of the fact that Leutheusser's model [which includes in the memory kernel, coupling to only $\phi^2(t)$] does not provide the stretching of the exponential in the long-time part of the decay (α relaxation) whereas Gotze and co-workers model [7] [which includes in the memory kernel, coupling to both $\phi(t)$ and $\phi^2(t)$ with different coupling constants] gives the stretching of the long-time decay. However without the inclusion of hopping both the models are valid only above the MCT transition temperature, T_c, whereas the stretching of the long-time part is only important below T_c. The origin of this stretching can both arise from MCT part of the dynamics as shown by Gotze and co-workers [6], and also from the hopping dynamics when the distribution of barrier heights are incorporated, as shown by Xia and Wolynes [10]. In the present work we as a first step towards unifying both the MCT and the hopping motion take the simpler model representing both the dynamics. That is, for MCT we consider the

Leutheusser model and for hopping dynamics we neglect the barrier height distribution. Thus although we will address the decay of the long-time part of the dynamic structure factor we will not address the stretching of the same.

As mentioned earlier MCT describes well the dynamics for a moderately supercooled system. It also works well for a deeply supercooled system confined within a single free energy minimum. These features are preserved when the hopping term or instanton vertex is added. In the idealized MCT, the equation of motion for the dynamic structure factor, $\phi^{\mathrm{id}}_{\mathrm{MCT}}(q,t)$ is first simplified by neglecting the coupling between different wave vectors and considering the contribution from the static and dynamic quantities at a single wave number, $q=q_m$ (q_m is the wave number where the peak of the structure factor appears). The idealized MCT equation according to Leutheusser model can be written as [4,5]

$$\ddot{\phi}^{\mathrm{id}}_{\mathrm{MCT}}(t) + \gamma\dot{\phi}^{\mathrm{id}}_{\mathrm{MCT}}(t) + \Omega_0^2\phi^{\mathrm{id}}_{\mathrm{MCT}}(t) + 4\lambda\Omega_0^2\int_0^t dt'\,\phi^{\mathrm{id}\,2}_{\mathrm{MCT}}(t')\,\dot{\phi}^{\mathrm{id}}_{\mathrm{MCT}}(t-t') = 0, \qquad (14)$$

where $\phi^{\mathrm{id}}_{\mathrm{MCT}}$ is the normalized density time correlation function. This integro-differential equation has an unusual structure but it can be solved numerically and many of its properties are now analytically understood. The frequency of the free oscillator can be approximated as $\Omega_0^2=k_BTq_m^2/mS(q_m)$ and the damping constant, γ, which is the short time part of the memory kernel, is taken to be proportional to Ω_0. This is because randomizing collisions occur in Lennard-Jones liquids on nearly the same time scale as the vibrations. The fourth term on the left-hand side has the form of a memory kernel and its strength is controlled by the dimensionless coupling constant which can be taken to be $\lambda=(q_mA^2/8\pi^2\rho)S(q_m)$, where $A\delta(q-q_m)=S(q)-1$, where only the first peak of $S(q)$ is considered [5]. It is useful to transform to the Laplace frequency plane, where the Laplace transform is defined as $\phi(s)=\mathcal{L}[\phi(t)]$. Now the equation can be rewritten as

$$\phi^{\mathrm{id}}_{\mathrm{MCT}}(s) = \frac{1}{s+\dfrac{\Omega_0^2}{s+\eta_l^{\mathrm{id}}(s)}}, \qquad (15)$$

where the longitudinal viscosity η_l^{id} is given by

$$\eta_l^{\mathrm{id}}(s) = \gamma + 4\lambda\Omega_0^2\mathcal{L}[\phi^{\mathrm{id}\,2}_{\mathrm{MCT}}(t)]. \qquad (16)$$

The above equations are nonlinear in nature and when Eq. (14) is solved numerically or Eqs. (15) and (16) are solved self-consistently for different values of λ, a dynamical arrest of the liquid structural relaxation is predicted at $T=T_c$ [4–6]. However, T_c is always higher than T_g. The origin for this inconsistency is the exclusion of the hopping motion in the perturbative MCT dynamics.

Hopping and continuous motion are essentially two distinct channels for the structural relaxation in a supercooled liquid, although they get coupled due to self-consistency, as described below. In the deeply supercooled regime these two styles of motion are usually well separated in their time scales. Exploiting this separation of time scales, the full intermediate scattering function can be written as a product of two functions [33],

$$\phi(q,t) \simeq \phi_{\mathrm{MCT}}(q,t)\phi_{\mathrm{hop}}(q,t), \qquad (17)$$

where $\phi_{\mathrm{MCT}}(q,t)$ is the mode coupling part and $\phi_{\mathrm{hop}}(q,t)$ is the contribution from the hopping motion, which is already discussed in the preceding section. While the above approximation should be regarded as phenomenological, later we show that such a form can indeed arise from a microscopic calculation.

We now derive the equation for $\phi_{\mathrm{MCT}}(q,t)$ which is consistent with Eq. (17). To begin with, note that the equation of motion for $\phi_{\mathrm{MCT}}(t)$ should remain the same as that for $\phi^{\mathrm{id}}_{\mathrm{MCT}}(t)$ [Eq. (14)]. However, due to the presence of hopping, the memory function will now be modified. According to MCT the longitudinal viscosity, which is the memory function, should be determined by the full dynamic structure factor which is given by Eq. (17). Therefore, $\phi_{\mathrm{MCT}}(t)$ is now solved self-consistently with the full dynamic structure factor, $\phi(t)$, and the equation of motion is written as

$$\ddot{\phi}_{\mathrm{MCT}}(t) + \gamma\dot{\phi}_{\mathrm{MCT}}(t) + \Omega_0^2\phi_{\mathrm{MCT}}(t) + 4\lambda\Omega_0^2 \times\int_0^t dt'\,\phi^2(t')\,\dot{\phi}_{\mathrm{MCT}}(t-t') = 0. \qquad (18)$$

Note that for simplicity we have removed explicit q dependence in the above equation and all the quantities are calculated at $q=q_m$. Although the structure of Eq. (14) and Eq. (18) are quite similar, the memory function in the former is calculated using only $\phi^{\mathrm{id}}_{\mathrm{MCT}}(t)$ whereas in the latter it is calculated using the full intermediate scattering function, $\phi(t)$. Thus $\phi_{\mathrm{MCT}}(t)$ is now dependent on the hopping motion. The equation in the Laplace frequency plane, for the modified $\phi_{\mathrm{MCT}}(s)$ remains the same as Eq. (15), except that the ideal longitudinal viscosity η_l^{id} is replaced by the following longitudinal viscosity given by

$$\eta_l(s) = \gamma + 4\lambda\Omega_0^2\mathcal{L}[\phi^2(\mathbf{t})]. \qquad (19)$$

We see at this order, the longitudinal viscosity is modified which in turn modifies the decay of $\phi_{\mathrm{MCT}}(t)$.

Combining Eq. (17) and Eq. (18) we can now write an equation of motion for the full structure factor, $\phi(t)$. The equation becomes simple when $\phi_{\mathrm{hop}}(t)$ can be approximated as an exponential with time scale $1/K_{\mathrm{hop}}$ that is $\phi_{\mathrm{hop}}(t)=\exp(-tK_{\mathrm{hop}})$. Now the equation of motion for $\phi(t)$ can be written as

$$\ddot{\phi}(t) + (\gamma+2K_{\mathrm{hop}})\dot{\phi}(t) + (K_{\mathrm{hop}}^2+\gamma K_{\mathrm{hop}}+\Omega_0^2)\phi(t) + 4\lambda\Omega_0^2 \times\int_0^t dt'\,\phi_{\mathrm{hop}}(t')\phi^2(t')[\dot{\phi}(t-t')+K_{\mathrm{hop}}\phi(t-t')] = 0. \qquad (20)$$

The effects of hopping motion in the full structural relaxation can be incorporated directly in the frequency plane which is suggested by Eqs. (10) and (15). Exploiting the strict parallelism of hopping and convective motion, these two equations can be combined to write an extended equation for the dynamic structure factor in the frequency plane as

$$\phi(\mathbf{s}) = \frac{1}{s + (v_0 - \Omega\hat{G}(q_m,s))P/v_p + \dfrac{\Omega_0^2}{s + \eta_l(s)}} = \frac{1}{s + K_{\text{hop}}(s) + K_{\text{MCT}}(s)}, \qquad (21)$$

where

$$K_{\text{hop}}(s) = (v_0 - \Omega\hat{G}(q_m,s))P/v_p$$

and

$$K_{\text{MCT}}(s) = \frac{\Omega_0^2}{s + \eta_l(s)} \qquad (22)$$

and $\eta_l(s)$ is given by Eq. (19). Note that even in this case in the calculation of the viscosity the full dynamic structure factor is used.

$K_{\text{MCT}}(s)$ and $K_{\text{hop}}(s)$ are the contributions to the rate of relaxation from MCT and hopping modes, respectively, and they act as two parallel channels for the decay of $\phi(t)$. At high temperature and low density $K_{\text{MCT}} \gg K_{\text{hop}}$, thus the decay of $\phi(t)$ is determined primarily by the MCT term. But as we approach T_c, the relaxation of $\phi(t)$ slows down which increases the longitudinal viscosity value [given by Eq. (16)]. This in turn causes $K_{\text{MCT}}(s)$ to decrease much faster than $K_{\text{hop}}(s)$ at low frequency. Now if we neglect the frequency dependence of K_{hop} then the equation of motion for $\phi(t)$ can be written as

$$\ddot{\phi}(t) + (\gamma + K_{\text{hop}})\dot{\phi}(t) + (\gamma K_{\text{hop}} + \Omega_0^2)\phi(t) + K_{\text{hop}}\delta(t) + 4\lambda\Omega_0^2\int_0^t dt'\,\phi^2(t')[\dot{\phi}(t-t') + K_{\text{hop}}\phi(t-t')] = 0. \qquad (23)$$

Note that as expected, while Eq. (23) has similar structure as Eq. (20), the memory function is different and the consequence of this will be discussed later.

The second scheme [given by Eq. (21)] appears to be rather similar to the extended mode coupling theory of Gotze and Sjogren [6,8]. In the extended MCT the current contribution is incorporated in the memory kernel. The modified memory kernel leads to an extra decay channel of the dynamic structure factor thus successfully predicting the decay of $\phi(t)$ below T_c. The rate of decay for the second channel, δ, is called the rate due to the hopping mode.

V. NUMERICAL CALCULATIONS AND RESULTS

For this paper Eqs. (14), (18), (20), and (23) are solved numerically. Although in principle Eqs. (21) and (22) can be solved self-consistently with Eq. (19) in an iterative way, it requires a very large number of iterations to converge near the glass transition temperature. An alternative way is to numerically solve Eq. (23). Both these calculations were done for a model system and for concreteness were applied to a specific molecular system, Salol.

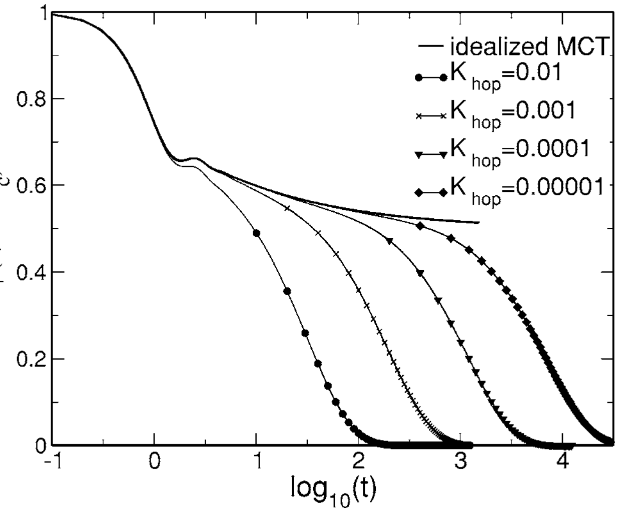

FIG. 1. The idealized MCT result [given by Eq. (14)] and the modified full $\phi(t)$ [given by Eq. (20)] have been plotted against $\log(t)$ for different values of K_{hop}. Time is scaled by picosecond. All the plots are for $\lambda=1$, that is at $T=T_c$, the mode coupling transition temperature. For different values of K_{hop} the curve follows the idealized MCT result until it starts decaying from the plateau. The smaller the K_{hop} value the longer the plateau and the slower the long-time decay.

A. Results for the schematic model

In the numerical calculations of the schematic model system, we took $\Omega_0=1$, and $\gamma=\Omega_0$ fixed. We varied λ between 0.1–1, knowing that T_c is reached for $\lambda=1$ and varied K_{hop} from 0.01 to 0.0001.

In Fig. 1 we plot both the idealized MCT result [given by Eq. (14)] and the modified full $\phi(t)$ [given by Eq. (17)] against $\log(t)$. We see that although the idealized MCT result saturates to a plateau value, the extended theory exhibits a hopping induced decay following the MCT plateau value—the duration of the plateau depends on the rate of hopping.

In Fig. 2 we plot the total $\phi(t)$ and $\phi_{\text{MCT}}(t)$ against time. The plot shows that hopping not only leads to the decay of the total $\phi(t)$ [given by Eq. (17)], but it also slows down the growth of the longitudinal viscosity thus facilitating the structural relaxation even through the mode coupling channel.

The long-time behavior of $\ln[\phi(t)]$ and $\ln[\phi_{\text{MCT}}(t)]$ are plotted against time in Fig. 3, for $\lambda=1$ and $K_{\text{hop}}=0.001$. The semilog plot shows straight lines in the long time with different slopes for the MCT part and the total dynamic structure factor, thus indicating that both the functions are exponential in the long time but with different time constants as evident in Fig. 2.

Next we compare the two different schemes at $T=T_c$ (that is, for $\lambda=1$) and for $K_{\text{hop}}=0.001$. In Fig. 4 we plot the solutions of Eqs. (20) and (23) against $\log(t)$. For comparison, in the same figure we also plot the solution of Eq. (17) where

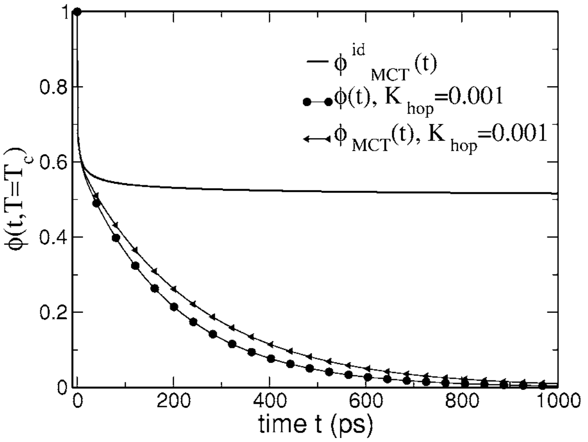

FIG. 2. The total $\phi(t)$ [given by Eq. (20)], the modified $\phi_{MCT}(t)$ [given by Eq. (18)] and the idealized $\phi^{id}_{MCT}(t)$ [given by Eq. (14)] are plotted against time for $\lambda=1$ (i.e., $T=T_c$) and for $K_{hop}=0.001$. After the initial short-time decay, both the total structural relaxation $\phi(t)$ and the MCT part of the structural relaxation $\phi_{MCT}(t)$ decays with time whereas the idealized MCT theory predicts no decay of the structural relaxation. This figure shows the decay of $\phi_{MCT}(t)$ due to hopping induced continuous diffusion in the system.

$\phi_{MCT}(t)$ is solved independently (non-self-consistently) using Eq. (14) (that is taking only the idealized MCT result). Both the self-consistent schemes provide similar results although the first scheme [Eq. (20)] shows a slightly faster decay implying that hopping has a stronger effect. A comparison between Eq. (20) and Eq. (23) shows that although the structures of the equations are similar, in the memory function of Eq. (20) there is an extra product with ϕ_{hop} which eventually leads to a faster decay of the total function, as seen in the figure. The solution of the non-self-consistent scheme [that is the solution of Eq. (17) where $\phi_{MCT}(t)$ is solved independently using Eq. (14)] shows an exponential decay from the plateau value with a time scale of $1/K_{hop}$.

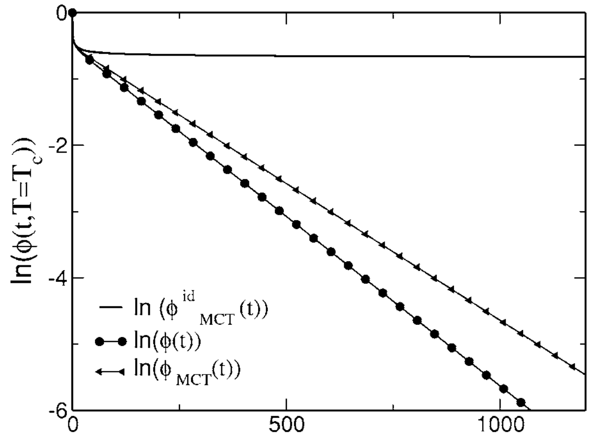

FIG. 3. $\ln[\phi(t)]$, $\ln[\phi_{MCT}(t)]$, and $\ln[\phi^{id}_{MCT}(t)]$ are plotted against time where the parameters are the same as in Fig. 2. The plots show that in the long-time both $\phi(t)$ and $\phi_{MCT}(t)$ decay exponentially with different time scales. Due to the presence of the explicit hopping term [see Eq. (17)] $\phi(t)$ decays faster than $\phi_{MCT}(t)$.

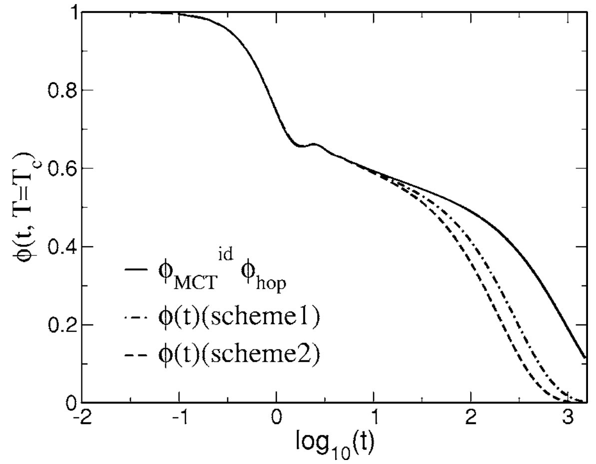

FIG. 4. To compare the two different approximate schemes, given by Eq. (20) (scheme 1) and by Eq. (23) (scheme 2) we plot $\phi(t)$ against $\log(t)$. Time is scaled by picosecond. For comparison, in the same figure we also plot the solution of Eq. (17) where $\phi_{MCT}(t)$ is solved independently (non-self-consistently) using Eq. (14) (that is taking only the idealized MCT result). The plots are for $\lambda=1$ (that is, at $T=T_c$) and $K_{hop}=0.001$. The non-self-consistent scheme gives a slower decay whereas both the self-consistent schemes show faster decay. This is because the hopping induces continuous diffusion in the system (see text for detailed discussion).

This decay is slower than that given by schemes 1 and 2 because in the non-self-consistent case the decay via the MCT channel is frozen whereas in the latter cases the MCT channel has its own time scale of decay. Thus self-consistent calculations show that hopping opens up continuous diffusion channels in the system. The advantage of the first scheme is that in this case we can separately calculate the MCT part of the dynamic structure factor and clearly demonstrate that hopping induces decay of ϕ_{MCT}. Although Fig. 4 suggests that similar dynamics is also present in scheme 2, due to the structure of the equation it is difficult to show it explicitly.

For further understanding the effect of hopping on the MCT dynamics (continuous diffusion), we plot $\phi(t)$ vs $\log(tK_{hop})$ [where $\phi(t)$ is obtained by solving Eq. (20) and Eq. (23)] for different K_{hop} values in Figs. 5 and 6, respectively. The plots would have produced a master curve in the long time (after the plateau) if the time scales of the long-time decay, τ_α, were equal to or linearly proportional to the respective $1/K_{hop}$ values. But, from Fig. 4 we have already concluded that due to the decay of the MCT part, τ_α is not equal to $1/K_{hop}$. Figures 5 and 6 further suggest that τ_α is not linearly proportional to $1/K_{hop}$. This is because in the self-consistent calculation the time scale of decay for $\phi_{MCT}(t)$ depends on $1/K_{hop}$ in a nonlinear manner.

In the schematic calculation we have independently varied λ and K_{hop} while keeping parameters Ω_0 and γ constant. In real systems all of these are functions of density and temperature and need to be varied simultaneously. Although the temperature dependence of Ω_0 and γ are not too strong, λ depends more strongly on T and K_{hop} is expected to have a stronger than exponential dependence on T. Thus for real systems, unlike as shown in Fig. 1, as the temperature is

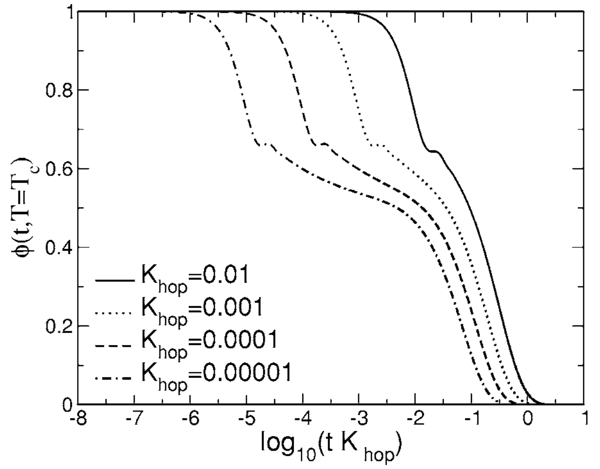

FIG. 5. The modified full $\phi(t)$ [given by Eq. (20)] is plotted against $\log(tK_{\text{hop}})$ for different values of K_{hop}. Time is scaled by picosecond. All the plots are for $\lambda=1$, that is at $T=T_c$, the mode coupling transition temperature. The plots show that the time scale of the long-time decay is faster than the hopping time scale which implies that other than the hopping motion there are other motions (namely diffusive motion) which relaxes the density correlation. The figure further suggests that the time scale of the diffusive motion is nonlinearly proportional to K_{hop}.

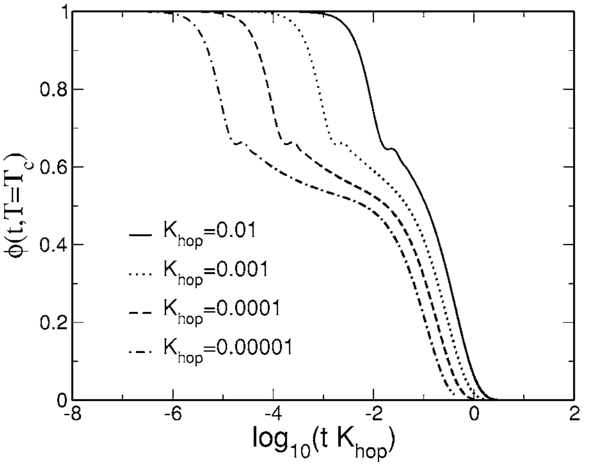

FIG. 6. The modified full $\phi(t)$ [given by Eq. (23)] is plotted against $\log(tK_{\text{hop}})$ for different values of K_{hop}. Time is scaled by picosecond. All the plots are for $\lambda=1$ that is at $T=T_c$, the mode coupling transition temperature. Similar to Fig. 5 the plots show that the time scale of the long-time decay is faster than the hopping time scale which implies that other than the hopping motion there are other motions (namely diffusive motion) which relaxes the density correlation. The figure further suggests that the time scale of the diffusive motion is nonlinearly proportional to K_{hop}.

lowered and the time scale of the long-time decay gets stretched, the λ value also increases leading to a higher value of the MCT plateau. In the next section we apply our theory to a real system chosen as Salol and include these effects.

B. Salol

Salol (phenyl salicylate) is a fragile glass forming substance. It is intramolecularly hydrogen bonded, a van der Waals system which is considered as a model substance for the study of glass transition and molecular mobility in the supercooled liquid. To perform the microscopic calculations, we need to map the system into a Lennard-Jones system and for that we need the molecular diameter and the well depth. Although the shape of the molecule is not spherical we can calculate an effective hard sphere diameter $\sigma_{\text{hs}}=7.22$ Å [34].

Note that in the RFOT theory the elementary particles in the system are not the molecules but beads and each molecule is made up of a certain number of beads. We thus need to estimate the bead size a. The RFOT theory predicts that a Salol molecule is made up of 6.29 beads [11]. Equating the volume of the molecule with the volume of 6.29 beads, we get the hard sphere bead size $a_{\text{hs}}=3.095$ Å which for the present calculation we equate to the Lennard-Jones bead size a. Next we need to estimate the temperature scaling which will be equivalent to the Lennard-Jones well depth ϵ. To obtain the temperature scaling we use the fact that for the reduced Lennard-Jones system the mode coupling transition is known to take place at reduced density, $\rho^*=0.95$ and reduced temperature, $T^*=0.57$. These values appear to be reasonable when compared with simulation results [19]. For a Salol system it is known that the mode coupling transition temperature, $T_c=256$ K [35], which should be proportional to the reduced temperature $T^*=0.57$ where the proportionality factor is the temperature scaling. Thus the temperature is to be scaled by $\epsilon/k_B=449.122$.

Now that we know the molecular and the thermodynamic parameters of the Lennard-Jones system, we can calculate the various parameter values in the integral equation that we need for a microscopic calculation, namely, for the MCT part, $\Omega_0^2=k_BTq_m^2/mS(q_m)$, γ and $\lambda=(q_mA^2/8\pi^2\rho)S(q_m)$, where $A\delta(q-q_m)=[S(q)-1]$, where only the first peak of the static structure factor is considered [5]. Instead of microscopically calculating the short-time part of the memory kernel, γ, we again take it to be proportional to Ω_0 with the proportionality factor assumed to be unity (as our schematic model study). Gotze and Sjogren [6] suggest that this proportionality factor even when varied between 1 and 100 does not affect the long time behavior. In the calculation of Ω_0 and λ, $S(q)$ is calculated for the above-mentioned Lennard-Jones system.

Next for the physical quantities in the hopping part of the calculation, we need to calculate ξ and P. These are temperature dependent quantities. For this calculation we use Eq. (13) where $T_A=333$ and $s_{\text{fit}}=2.65$ [11]. Once we get the ξ and P values we can calculate the hopping relaxation kernel K_{hop} from Eq. (12). The values for all the calculated parameters are given in Table I. Note that T_A is higher than the melting temperature, $T_m=315$. This can be rationalized using the landscape picture [36].

The plot for the Salol system obtained by using the parameters reported in Table I is given in Fig. 7. The plot appears to be quite similar to Fig. 1. Due to the presence of hopping the structural relaxation decays from the plateau value even below the mode coupling transition temperature, $T_c=256$ K. From Table I we find that Ω_0 and γ have a weak temperature dependence which is reflected in Fig. 7 in the

TABLE I. In this table we present the value of the parameters calculated. Ω_0 is the frequency of the free oscillator, γ is the short-time part of the memory function, acting as a damping constant. λ provides an estimate of the strength of coupling and is a dimensionless quantity. ξ is the radius of the region of hopping, $(v_0-\Omega\hat{G}(q_m))/v_p$ gives the effect of a single hopping on the density, P is the hopping rate per particle and K_{hop} is the hopping relaxation kernel calculated from Eq. (12) (or essentially the product of the sixth and seventh column). We find that Ω_0 and γ have a weak temperature dependence which implies that the short-time dynamics remain unchanged. Although, λ also shows a weak temperature dependence but a small variation in λ leads to a substantial change in the dynamics. The hopping rate varies strongly with temperature.

T(K)	Ω_0^2(ps^{-2})	γ(ps^{-1})	λ	ξ/a	$\dfrac{(v_0-\Omega\hat{G}(q_m))}{v_p}$	P(ps^{-1})	K_{hop}
270	1.353	1.163	0.94	1.89	1.79	3.09×10^{-4}	5.53×10^{-4}
256	1.268	1.126	1.01	2.32	3.47	3.2×10^{-7}	1.11×10^{-6}
247	1.216	1.102	1.05	2.62	5.12	2.89×10^{-8}	1.48×10^{-7}

near invariance of the short-time dynamics at all three temperatures. On the other hand, λ shows a weak temperature dependence but a small variation in λ leads to a substantial change in the dynamics. Above $\lambda=1$ the increase in its magnitude leads to an increase of the plateau value. The hopping rate varies strongly with temperature and has a stronger effect on the dynamics above $\lambda=1$. At lower temperatures as the hopping rate decreases the plateau is stretched to longer times. Below $\lambda=1$ (or $T>T_c$), where $\phi(t)$ can decay completely via the diffusive channel (MCT part), the presence of hopping leads to a slightly faster decay of the structural relaxation.

VI. CONCLUDING REMARKS

Experiments show that the structural relaxation in a supercooled liquid exhibits rich dynamics over many time and length scales. Often the physical origin of these different dynamics are quite disparate. To explain the dynamics of the liquid over the whole temperature regime under a single theoretical framework has been a challenge. The random first order transition theory which at high temperature also contains the essential elements described in the perturbative mode coupling theory [17] has been successful in explaining the liquid dynamics around the laboratory glass transition temperature T_g. The mode coupling theory, on the other hand, has been able to explain the high temperature dynamics extremely well. The theory is also known to be accurate for short times in the supercooled liquid below T_c. Below T_c on long time scales the idealized MCT theory fails because of the exclusion of the activated hopping motion. On the other hand, RFOT theory provides a quantitative description of these hopping motions in terms of instantons. Therefore, in this work we have proposed a unification of these two theories to provide a dynamical description of the liquid, covering the whole temperature regime, from above T_c to T_K.

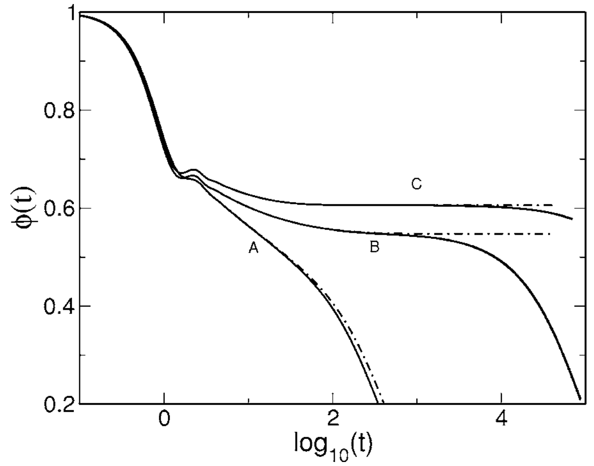

FIG. 7. The calculated structural relaxation for Salol at three state points (which also includes the mode coupling transition temperature T_c=256 K) against log(t). Time is scaled by picosecond. Equation (20) is solved with the parameters given in Table I to obtain $\phi(t)$. The solid lines A, B, and C correspond to $\phi(t)$ at temperatures 270 K, 256 K, and 247 K, respectively. The dotted-dashed lines are the plots at the same temperatures but without hopping (that is, the idealized MCT result).

Towards this goal we first treated the effect of hopping on the density fluctuation. In the theory the effect of a single particle hopping is connected to the neighboring density fluctuations through a propagator. The typical rate of a particle hopping and the spatial extent of a hopping event are obtained from RFOT theory. After incorporating all the information it is found that hopping acts as a channel for the decay of the structural relaxation [Eq. (10)]. Distribution of hopping times are essential for the nonexponentiality of the α relaxation [12] and will be incorporated in future work. On the other hand, the distribution of hopping rate or the distribution of barrier height is connected to the jump in the specific heat capacity through the configurational entropy [10]. Thus it should be also possible to correlate the kinetic anomalies (like stretching of the relaxation time) with the thermodynamic anomalies (jump in the heat capacity) as has been observed in the experiment [24].

The total structural relaxation after incorporating the hopping motion was calculated using two different approximate schemes. As in idealized MCT, the density relaxation is calculated self-consistently with the longitudinal viscosity. It is found that due to the inclusion of hopping motion the arrest of the structural relaxation at T_c, as predicted by the idealized MCT, disappears. The self-consistent nature of the calculation lead to the hopping induced softening of the growth of frequency dependent viscosity and this in turn helps the relaxation of the MCT part of the dynamic structure factor. Thus the study predicts that below T_c, hopping not only relaxes the total density correlation but also invokes a decay of the otherwise frozen MCT part of the dynamic structure factor. This implies that hopping opens up continuous diffusion channels in the system. This is consistent with the coexistence of both kinds of motions observed in computer simulation [19]. It is also found that due to the self-consistent calculation the effect of hopping on the MCT dynamics is nonlinear in nature. Note that the two schemes proposed in this paper to incorporate the hopping motion in the total structural relaxation lead to equations that are similar to the equations obtained from microscopic approaches [6,25]. However, there can obiviously be other similar schemes to incorporate the hopping motion.

It is interesting to consider the predictions of the present generalized theory regarding the temperature dependence of viscosity. The decay of the MCT part of the dynamic structure factor already predicts a slower rise of the viscosity with the temperature than the ideal MCT. The interesting point to note is that the hopping rate itself also decreases with the lowering of temperature. Thus, the dynamic structure factor now not only has a slow exponential decay in the long time, but the plateau also gets stretched to longer times. Both the slow exponential relaxation at long times and the stretching of the plateau at intermediate times contribute to the increase of the viscosity. However, the resulting temperature dependence can be quite different from the prediction of the ideal MCT.

ACKNOWLEDGMENTS

This work was supported in part by NSF (USA) and DST (India). The authors thank M. Ediger, M. K. Mapes, and D. Chakrabarti for helpful discussions.

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[36] It is well known that $T_g \simeq 2/3 T_m$ [cf. see F. H. Stillinger, Science **267**, 1935 (1995) and C. A. Angell *et al.*, J. Appl. Phys. **88**, 3113 (2000)]. We also know that $T_c \simeq 1.2 T_g$ [cf. see A. P. Sokolov, W. Steffen, and E. Rossel, J. Phys.: Con-

dens. Matter **8**, 9587 (1996)]. Thus $T_c \simeq 0.8T_m$. According to RFOT, T_A should be viewed as the temperature where the barrier disappears when approached from below or rather the temperature where the barrier appears when approached from above. According to the landscape picture the energy starts falling from $T^* \simeq 1.0$ and one expects the energy landscape to exert an influence on the dynamics (cf. see S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature **393**, 554 (1998)]. Thus we can say that $T_A^* \leqslant 1.0$, which is much higher than $T_c^* \simeq 0.435$ and thus also higher than T_m^* which is consistent with the discussions presented in the paper.