

Subquadratic wavenumber dependence of the structural relaxation of supercooled liquid in the crossover regime

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As a liquid is progressively supercooled toward its glass transition temperature, an intriguing weakening of the wavenumber (q) dependence of the structural relaxation time $\tau(q)$ in the intermediate-to-large q limit is observed both in experiments and simulation studies. Neither continuous Brownian diffusive dynamics nor discontinuous activated events can alone explain the anomalous wavenumber dependence. Here we use our recently developed theory that unifies the mode coupling theory for continuous dynamics, with the random first order transition theory treatment of activated discontinuous motion as a nucleationlike instanton process to understand the wavenumber dependence of density relaxation. The predicted smooth change in mechanism of relaxation from diffusive to activated, in the crossover regime, is wavevector dependent and appears to be responsible for the observed subquadratic, almost linear, q dependence of the relaxation time. © 2010 American Institute of Physics. [doi:10.1063/1.3330911]

I. INTRODUCTION

In deeply supercooled liquids, there is an interesting crossover in dynamics from continuous (in space) small amplitude Brownian movement of particles to rare, nearly discontinuous, larger amplitude hopping motions. This crossover occurs over a range of temperature which is limited on one side by the temperature (T_L) that signifies the onset of nonzero free energy barriers for motion in the inherent structures, and ultimately by the glass transition temperature on the other side when the system falls out of equilibrium, as shown by Bhattacharyya, Bagchi, and Wolynes (BBW).¹ It has been shown that this onset temperature T_L (Ref. 2) coincides with the ideal mode coupling theory (MCT) transition temperature T_c^o .³ In Salol, the range is found to be between 278 and about 240 K. Above 278 K, continuous Brownian diffusion dominates while below 240 K, hopping motion is found to control the mass transport.¹

Diffusion in an equilibrated supercooled liquid, whatever the mechanism of transport at the microscopic level, should follow Fick's law at long length scales and therefore, the relaxation time should exhibit a quadratic q dependence at small q . Thus long time and long wavelength diffusion is in any event, insensitive to the details of the mass transport or relaxation mechanism present in the crossover region. But at intermediate to large q , structural relaxation becomes sensitive to the gradually changing mechanism and thus provides a highly useful window to probe the details of the relaxation dynamics.

A characteristic feature of the dynamics in supercooled liquids is a pronounced nonexponential relaxation of the long

time decay, commonly known as the α -relaxation. This relaxation is usually fitted to the Kohlrausch–William–Watts (KWW) function,

$$\phi(q,t) = f(q)e^{-(t/\tau(q))\beta(q)}, \quad (1)$$

where $f(q)$, $\tau(q)$, and $\beta(q)$ are the wavenumber dependent nonergodicity parameter, the relaxation time, and the stretching parameter, respectively. This functional form exhibits highly nontrivial q dependence. When $\phi(q,t)$ denotes the density correlator, then $f(q)$, $\tau(q)$, and $\beta(q)$ all oscillate in phase with the static structure factor, $S(q)$. Although all the oscillations are in phase with $S(q)$, each parameter exhibits different q dependence. In the simulation studies of Tartaglia and co-workers on water^{4,5} and ortho-terphenyl (OTP),⁶ the variation of $\tau(q)$ of the self and the collective density correlator with q at different temperatures was studied. In their study in the large q limit, as the temperature is lowered, the q dependence of $\tau(q)$ shows a crossover from the expected quadratic to an unexpected linear behavior, $\tau(q) \propto q^{-\alpha}$, where $\alpha=2$ in the small q limit and $\alpha \approx 1$ in the large q limit at low temperatures.⁴ Similar subquadratic q dependence at low temperature has been observed in Brownian dynamics study of hard spheres.⁷ In a different simulation study on polymer melt, the q dependence of $\tau(q)$ was studied at three different temperatures.⁸ In the large q limit, when the data was fitted to MCT prediction,⁹ $\tau(q) \propto q^{-1/b}$ (where b is the von-Schweidler's exponent), a value of $b=0.75$ was obtained, which implies that $\tau(q)$ has a weaker than quadratic q dependence. A careful analysis of the data reveals a further weakening in the q dependence of $\tau(q)$ with lowering of T . Experimental study of aging in clay suspension also reports a linear q dependence of the relaxation time.¹⁰

Chong¹¹ has discussed q -dependent relaxation treating the effects of the activated hopping on MCT dynamics in a

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spirit similar to BBW.¹ However, Chong's treatment of the activated hopping is different from the present one in several respects. Chong considers the jump or hopping motion to be a single particle movement in the spirit similar to the diffusion-jump processes of defects often considered in crystals.¹² In deeply supercooled liquids, individual jump motions are rare and the relevant reaction coordinate must involve many particles, as indeed has been observed in several computer simulation studies.¹³ The single particle activated picture also is inconsistent with measurements and influences of the dynamical correlation length in deeply supercooled liquids. In BBW, the activated motion occurs via nucleation of a mobile liquid phase from a frozen amorphous phase and a region of the size of a dynamical correlation length, determined by the instanton structure,¹⁴ is affected. In addition, within the random first order transition theory (RFOT) theory, the barrier height distribution is a function of configuration entropy and its fluctuation.¹⁵ Moreover, the apparent barrier height distribution gets renormalized by the MCT dynamics.¹ In Chong's treatment of the activation barrier, the relationship between entropy and barrier height is left open and activation is treated as an adjustable parameter.¹¹

Saltzman and Schweizer⁷ have also considered q -dependent structural relaxation to occur through a barrier crossing dynamics and the barrier they use is obtained from density functional theory in the spirit similar to Singh *et al.*¹⁶ However, the treatment of Saltzman and Schweizer⁷ does not fully consider the interplay between the activated dynamics and the continuous motion within any analytical framework, although the effects of such interplay should be present in their Brownian dynamics simulation. Unfortunately again, their analytical treatment is at a single particle level, thus failing to account for the correlated nature of dynamics in supercooled regime.

Both Chong¹¹ and Saltzman and Schweizer⁷ have studied the temperature dependence of the length scale above which Fickian diffusion sets in but neither treatment addresses the wavenumber dependence in the non-Fickian regime (where $\tau(q) \propto q^{-\alpha}$, α decreases as the temperature is lowered) and how α is related to the activated dynamics. The phenomenon of the weakening of the q dependence of $\tau(q)$ at large q is often attributed to activated hopping dynamics alone.¹⁷ It should be pointed out that within the single particle jump diffusion model a much weaker q dependence is predicted in the large q limit, a point which is not often appreciated. In addition, the jump diffusion model also does not account for the nontrivial temperature dependence of the exponent α .¹⁸

As mentioned earlier, the dynamics in the supercooled liquid regime, near a temperature substantially above the laboratory glass transition temperature, undergoes a rather smooth change from continuous to activated motion and in the crossover region both the mechanisms of relaxations are present.¹ Intriguingly, the progressive weakening of the wavenumber dependence of the relaxation time occurs in this same temperature regime. However, a quantitative correlation between the two phenomena has not yet been fully established.

This article addresses this problem by extending our recently developed unified theory^{1,19} to the full wavevector plane. We will see that an explanation of the wavenumber dependence of $\tau(q)$ requires the dynamics to have contributions from both diffusive and activated dynamics as well as an interaction between these two different dynamics which leads to hopping induced diffusion. The change of mechanism of transportation (crossover) is wavenumber dependent giving rise to the gradual weakening of the q dependence of the relaxation time. We report here results for the coherent intermediate scattering function, $\phi(q, t)$ but in the large q limit where apart from the modulation of $\tau(q)$ by the structure factor, $S(q)$, the timescale of both the total (coherent) and the self (coherent) intermediate scattering functions show similar q dependence.

II. THEORETICAL SCHEME

The previously developed theoretical scheme that combines the hopping (through RFOT theory) and continuous diffusive (described using MCT) dynamics can be applied to study the wavenumber dependence of the various dynamical quantities as described below. The main point is that MCT treats perturbative effects on the motion while activated events are rare involving far from typical trajectories. The most probable activated event is an instanton of the nonlinearly averaged equation.

Let us suppose an instanton pops up at a position R . In a very brief time, the particles within the sphere of radius ξ around the position R will be displaced by a Lindemann length, d_l . Now the equation describing the change in density $\rho(r)$ due to a single instanton popping up and while the density field still undergoes continuous diffusive dynamics can be written as

$$\begin{aligned} \delta\rho(\mathbf{r}, t + \delta t) &= \delta\rho(\mathbf{r}, t) + P_{\text{hop}}^{\text{total}} \delta t \frac{1}{V} \int d\mathbf{R} \theta(\mathbf{r} - \mathbf{R}) < \xi) \\ &\times \left[\int dt' \int_{\mathcal{D}(R)} d\mathbf{r}' \delta\rho(\mathbf{r}', t') \times G(\mathbf{r}, \mathbf{r}', t - t') \right. \\ &\left. - \delta\rho(\mathbf{r}, t) \right] - \delta t \int dt' \int d\mathbf{r}' \delta\rho(\mathbf{r}', t') K_{\text{MCT}}(\mathbf{r}, \mathbf{r}', t - t'), \end{aligned} \quad (2)$$

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 Green's function which determines the effect of instanton in moving particles from position \mathbf{r} to a new one \mathbf{r}' , typically a Lindemann length away, during time t and $t + \delta t$. $\mathcal{D}(R)$ determines the region where the effect of the instanton is felt.¹⁹ $P_{\text{hop}}^{\text{total}}$ is the total rate of a hopping in the volume V . K_{MCT} is the diffusive kernel which represents the diffusive dynamics as described by MCT.^{1,19}

From Eq. (2), the total scattering function can be written as¹⁹

$$\phi(q, z) = \frac{1}{z + K_R(q, z)}, \quad (3)$$

where $K_R(q, z) = K_{\text{hop}}(q, z) + K_{\text{MCT}}(q, z)$ describes the renormalized kernel describing both the activated and the diffusive dynamics. However, this form of the MCT-RFOT equation does not allow one obviously to separate the contributions from the diffusive and activated motions. Thus, to describe the total intermediate scattering function, we use an approximate form of the equation using an approximation^{1,19,20}

$$\phi(q, t) \approx \phi_{\text{MCT}}(q, t) \phi_{\text{hop}}^{\text{static}}(q, t). \quad (4)$$

It has been demonstrated elsewhere that the results obtained for $\phi(q, t)$ from Eqs. (3) and (4) have very similar form and describe similar dynamics.¹⁹ As mentioned earlier, the advantage of describing $\phi(q, t)$ using Eq. (4) is that we can now separately analyze the activated and the MCT parts of the total dynamics.

In describing the activated dynamics, we must account for the fact that there is a distribution of the hopping barriers in the system. These arise from the entropy fluctuation.¹⁵ When there is a multiplicity of barrier hopping events one can write,

$$\phi_{\text{hop}}^{\text{static}}(q, t) = \int \phi_{\text{hop}}^{\text{single}}(q, t) \mathcal{P}^{\text{static}}(\Delta F) d\Delta F, \quad (5)$$

where the $\mathcal{P}^{\text{static}}(\Delta F)$ that arises from configurational entropy fluctuations is approximately Gaussian when the reconfiguring region is large,

$$\mathcal{P}^{\text{static}}(\Delta F) = \frac{1}{\sqrt{2\pi(\delta\Delta F)^2}} e^{-(\Delta F - \Delta F_o)/2(\delta\Delta F)^2}. \quad (6)$$

We call this distribution ‘‘the static barrier height distribution.’’ $\phi_{\text{hop}}^{\text{single}}(q, t)$ describes the activated hopping dynamics for a single hopping barrier and has been derived in an earlier paper,¹⁹ and in the frequency (z) plane, it is written as,

$$\phi_{\text{hop}}^{\text{single}}(q, z) = \frac{1}{z + K_{\text{hop}}(q, \Delta F)}, \quad (7)$$

where ΔF is the free energy barrier for hopping. The expression of the hopping kernel, K_{hop} is assumed to be independent of time and also a function of the free energy barrier,

$$K_{\text{hop}}(q, \Delta F) = \frac{P_{\text{hop}} v_0}{v_p} [1 - G(q)], \quad (8)$$

where $P_{\text{hop}} = P_{\text{hop}}^{\text{total}}/V$ is the average hopping rate which is a function of the free energy barrier height, ΔF , and is given by $P_{\text{hop}} = (1/\tau_0) \exp(-\Delta F/k_B T)$.¹⁴ The free energy barrier is calculated from RFOT theory.¹⁴ $v_0 = \frac{4}{3} \pi \xi^3$ is the region participating in hopping where the correlation length ξ is calculated from RFOT theory. v_p is the volume of a single particle in the system. d_L is the Lindemann length.

Supercooled liquid simulation studies have shown that there is in fact not a single length but rather a distribution of jump lengths which can be fitted to an exponential distribution.²¹ This would presumably be found from the detailed solution of the time dependent instanton equations.

The most probable jump length has been found to be of the order of Lindemann length with the value decreasing as the temperature is lowered. In this work, we will take the distribution of jump lengths, $f_o(l)$, to be given by

$$f_o(l) = l l_o^{-2} \exp(-l/l_o), \quad (9)$$

so that the Green’s function can then be written as

$$G(q) = \frac{1}{1 + q^2 l_o^2}, \quad (10)$$

where l_o is the most probable jump length which is found to be close to the Lindemann length. The hopping kernel can be written as

$$K_{\text{hop}}(q, \Delta F) = \frac{P_{\text{hop}} v_0}{v_p} \left(\frac{q^2 l_o^2}{1 + q^2 l_o^2} \right). \quad (11)$$

We now write the equation of motion for the MCT part of the intermediate scattering function, $\phi_{\text{MCT}}(q, t)$ which is now self consistently calculated with $\phi(q, t)$,

$$\begin{aligned} \ddot{\phi}_{\text{MCT}}(q, t) + \gamma_q \dot{\phi}_{\text{MCT}}(q, t) + \Omega_q^2 \phi_{\text{MCT}}(q, t) \\ + \int_0^t dt' \Omega_q^2 \mathbf{m}_q(t') \dot{\phi}_{\text{MCT}}(q, t - t') = 0. \end{aligned} \quad (12)$$

The memory function m_q is a function of M variables $\phi(q, t)$, ($q=1, 2, \dots, M$) and is given by

$$\begin{aligned} \mathbf{m}_q(t) &= \mathcal{F}_q(\phi(t)) \\ &= \sum_{\vec{k} + \vec{p} = \vec{q}} V(\vec{q}; \vec{k}, \vec{p}) \phi(k, t) \phi(p, t) \\ &= \sum_{\vec{k} + \vec{p} = \vec{q}} [\rho S(q) S(k) S(p) \{ \vec{q} \vec{k} c(k) \\ &\quad + \vec{p} c(p) \}]^2 / 2q^4] \phi(k, t) \phi(p, t), \end{aligned} \quad (13)$$

where \mathcal{F}_q is the mode coupling functional. The vertices V are equilibrium quantities.²² In our numerical work the double summation in Eq. (13) is approximated by a Riemann sum,²² where $M=100$ and the cutoff wavevector $q^{\text{cutoff}} = 40.0$.

A. Results

We first discuss the choice of parameters. Following our earlier work, we have taken the thermodynamic conditions appropriate for Salol, although the calculations are quite general. The system at high temperature is chosen to be just above the idealized MCT transition having $T=280$ K, $\rho^* = 0.99$ and the lowest temperature $T=229$ K, $\rho^* = 1.27$. The last value is suggested by the simulation studies²³ of deeply supercooled liquids with model Lennard-Jones potential, which shows that at $\rho^* = 1.27$, $T^* = 0.5$ the system is highly viscous. In van der Waals systems, the large change in density drives the caging which can in principal arise not only due to change in density but due to transient bond formation, which happens in many systems such as water. Since we do not explicitly take into consideration the other sources of caging, so in a mean-field way, to mimic strong caging, the density is increased by a large amount. The density between $T=280$ K and $T=229$ K is calibrated in a linear fashion.

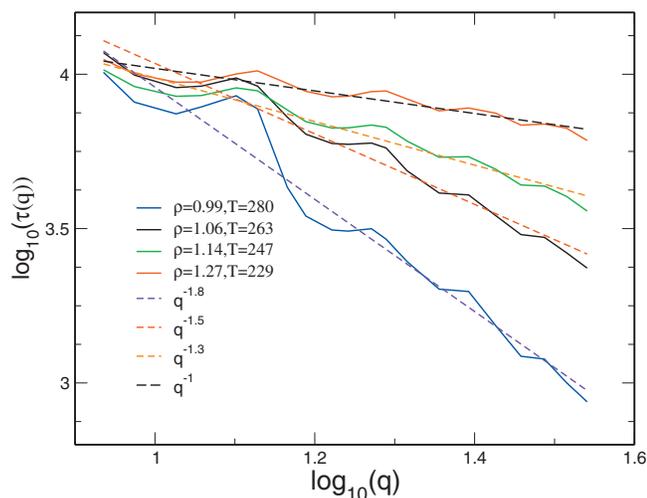


FIG. 1. The α relaxation timescale $\tau(q)$ plotted as a function of q at different densities and temperatures. The $\tau(q)$ values are scaled such that at $q = 8.6$ they have similar values. $\tau(q)$ shows a weaker q dependence as the temperature is lowered.

With these values, we calculate the structure factor using the Percus–Yevik approximation with correction. The structure factor is used in the calculation of the microscopic MCT vertex. The parameters required to calculate the activated dynamics for this system were discussed extensively in Ref. 1.

With the above mentioned parameters, $\phi(q, t)$ is calculated at different wavenumbers, q , and over the full time domain t . Numerical calculations were carried out using the scheme given in Ref. 24. The longtime part of $\phi(q, t)$ at each wavenumber is fitted to the KWW function [Eq. (1)], where all the KWW parameters, the form factor, $f(q)$, the relaxation time, $\tau(q)$ and the stretching parameter, $\beta(q)$ are varied to get the fit. Similarly $\phi_{\text{MCT}}(q, t)$ and $\phi_{\text{hop}}(q, t)$ are also fitted to KWW function to obtain the corresponding MCT and activated dynamics parameters.

The fitting parameter from this theory are easily displayed. $\log_{10} \tau(q)$ is plotted against $\log_{10}(q)$ at four different temperatures (Fig. 1). As the temperature is lowered, the wavenumber dependence of the relaxation time gradually becomes weak, much as is observed in simulations and experiments on the coherent and incoherent scattering functions.^{4–8} There can be two possible origin of such weakening of wavenumber dependence. First, it can be that the relaxation time of the MCT dynamics (at low temperature it can be hopping induced diffusion) gets modified and itself shows a weaker than quadratic wavenumber dependence. The second possibility is that in this temperature regime as observed earlier¹ the total dynamics is describe both by the MCT and the activated dynamics and their interplay and this gives rise to a wavenumber dependence, which is neither characteristic of purely diffusive nor purely activated dynamics.

To check the first possibility in Fig. 2, the total relaxation time, τ_{total} , the hopping induced MCT relaxation time, τ_{MCT} and the relaxation time of the activated hopping dynamics, τ_{hop} in the large q regime are plotted at three different temperatures. In the large q regime, the hopping induced MCT relaxation time, $\tau_{\text{MCT}}(q)$, at all the temperatures, as

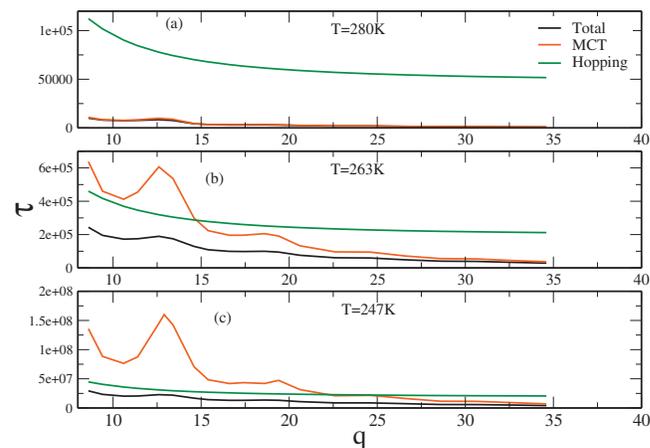


FIG. 2. (a) The total relaxation time, τ_{total} , the hopping induced MCT relaxation time, τ_{MCT} , and the relaxation time of the activated hopping dynamics, τ_{hop} , are plotted against wavenumber, q at $T=280$ K and $\rho^*=0.99$. The total relaxation is primarily determined by the hopping induced diffusive dynamics. (b) Same as in (a) but at $T=263$ K and $\rho^*=1.06$. The τ_{total} in the intermediate wavenumber is primarily determined by the hopping dynamics whereas in the large q regime the τ_{total} follows τ_{MCT} . (c) Same as in (a) but at $T=247$ K and $\rho^*=1.14$. Here too the total relaxation in the intermediate wavenumber is primarily determined by the hopping dynamics and only in the very large wavevector regime MCT plays a dominant role.

observed in the case of idealized MCT,²⁵ shows a quadratic q dependence whereas $\tau_{\text{hop}}(q)$ as expected is almost independent of q . As discussed earlier, the quadratic wavenumber dependence ($\tau(q) \propto 1/q^2$) is a signature of the continuous Brownian diffusion and the weak wavenumber dependence ($\tau(q) \propto 1/q^\alpha$) is a signature of discontinuous activated hopping.

An interesting observation here is that, even at low temperatures below T_c^o , the hopping induced diffusive dynamics is found to be strongly wavenumber dependent although the hopping dynamics itself has a weak wavenumber dependence (Fig. 2). An asymptotic analysis of the MCT dynamics allows one to extract the timescale of the MCT dynamics below T_c^o , neglecting the coupling between wavenumbers, $\tau_{\text{MCT}}^{-1} = (2\tau_{\text{hop}}^{-1}) / [\lambda(q)f(q)^2 - 1]$.²⁶ Here $f(q)$ denotes the form factor or the Debye–Waller factor (DWF). $\lambda(q)$ denotes the coupling strength of the self coupling term and is a function of $m_q(t=0)$. The relation will be more complex for the present more complete treatment where all the wavenumbers are coupled. However, even in the decoupled limit, at large q , although τ_{hop} is independent of q , the hopping induced diffusive dynamics has a q dependence and the relaxation time is longer for wavenumbers where the DWF is larger.

Since we find that hopping induced MCT contribution at all temperatures retains its wavenumber dependence and the activated dynamics at large q is almost independent of wavenumber, thus neither MCT nor activated dynamics alone will explain the subquadratic, almost linear, wavenumber dependence of the relaxation time. At high T , for all q , as discussed earlier, the dynamics is primarily determined by MCT [Fig. 2(a)]. In the large wavenumber regime, even at low T both MCT and activated dynamics have competing timescales and the relaxation has contributions from both. However, at low T and in the intermediate wavenumber regime, the MCT relaxation time becomes very slow (due to caging effect or

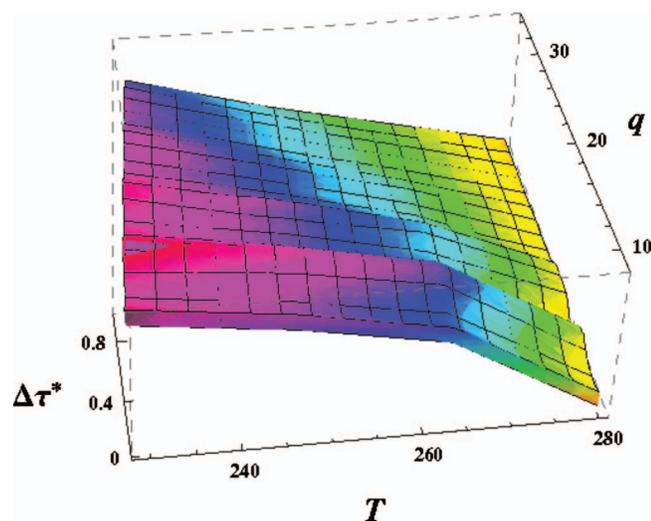


FIG. 3. Wavenumber dependent crossover to the activated regime. The function $\Delta\tau^* = (\tau_{\text{MCT}} - \tau_{\text{total}}) / \tau_{\text{MCT}}$ is plotted against both temperature and wavenumber. The closer the value of the function to unity the more is the effect of activated dynamics. In the intermediate wavenumbers, the crossover to the activated dynamics dominated regime is sharper and takes place at a higher temperature. In the large q regime, this crossover takes place over a wide temperature range.

large DWF) thus the relaxation primarily occurs via activated dynamics. Thus in this regime, the growth of relaxation time with lowering of q is not as strong (quadratic) as predicted by the MCT dynamics.

In an earlier study, it was shown by plotting $\Delta\tau^* = (\tau_{\text{MCT}}(q) - \tau_{\text{total}}(q)) / \tau_{\text{total}}(q)$ against temperature that there is no abrupt change in the dynamics from diffusive to activated, and that the change is rather gradual and there is a crossover regime.¹

It is interesting to note that the two different regimes in the crossover region can be identified with two regimes already well known in the energy landscape paradigm.² At the high temperature side of the crossover region is the landscape influenced regime where the hopping begins to make its presence felt, still mainly through the hopping induced MCT term. On the other hand, at the low temperature side of the crossover, we can identify the landscape dominated regime where relaxation is fully determined by the activated dynamics. Here this crossover is investigated in the full wavenumber domain. $\Delta\tau^*$ is plotted as a function of both temperature and wavenumber in Fig. 3. The higher the value of this function the stronger is the effect of hopping. At high temperature, over the whole wavenumber regime, the effect of activated dynamics is very weak. As the temperature is lowered, the effect of the activated dynamics shows strong wavenumber dependence. In the intermediate q regime, the crossover is sharper and takes place at a comparatively higher temperature. In the large q regime, the crossover is quite gradual. Thus there is a q dependence of the crossover, which is also evident from Fig. 2, which essentially gives rise to the gradual weakening of the q dependence of the relaxation time.

The range of the subquadratic behavior primarily positioned in the intermediate wavenumber regime becomes asymmetrically wider as the temperature is lowered. As ob-

served in Figs. 2 and 3, the effects of hopping dominated regime extends to higher q values with lowering of T . Thus the subquadratic regime also extends to higher values of q .

B. Discussion

The unusual wavenumber dependence of the relaxation time observed in supercooled liquids and its connection to the crossover dynamics has heretofore remained largely unexplored.⁴⁻⁸ This article addresses this problem by extending the bridged theory^{1,19} to the full wavevector plane. We show that the full wavevector dependent unified theory explains the gradual weakening of wavenumber dependence of the relaxation time as the temperature is lowered. The theory predicts that for systems where the caging effect grows strongly with lowering of temperature, the MCT relaxation time in the intermediate wavevector regime slows down faster and the crossover to the activated dynamics dominated regime happens earlier. We have shown that this crossover to the purely activated regime is strongly wavenumber and temperature dependent. The crossover to the activated regime happens earlier at intermediate wavenumbers, whereas at the same temperature and at larger wavenumbers, the MCT contribution still remains substantial. Because of this wavenumber dependent crossover, the relaxation time at low T is governed mostly by activated dynamics at intermediate q and both by activated and MCT dynamics at larger q . Hence the relaxation time does not grow as strongly with lowering of q as expected from only the diffusive MCT dynamics.

The theory also predicts that if the caging effect is not so strong so as to significantly slow down the MCT dynamics (compared to hopping), we should observe quadratic wavenumber dependence even at lower temperature. The analysis also reveals that for systems where the caging effect is stronger, the transition from MCT dominated regime to the activated dynamics dominated regime should be sharper. This would mean that the phenomenological MCT transition temperature, T_c^{fit} will appear to be close to the microscopic MCT transition temperature T_c^0 . In other cases where the caging effect is not very strong or does not grow very fast upon cooling, the transition takes place over a wider temperature regime and the separation between T_c^{fit} and T_c^0 should be wider.

The present analysis suggests that while a growing correlation length is essential to describe the timescale of activated dynamics and thus the subquadratic q dependence is related to ξ , there appears to be no one-to-one relation between them. The subquadratic q dependence is not described by activated dynamics alone but it is the MCT and the activated dynamics and their interplay that give rise to this phenomenon. Since MCT dynamics is independent of ξ and depends on many other local factors such as caging, the relationship between the correlation length ξ and the subquadratic wavenumber dependence may not be universal. For the system studied, it is fair to say that subquadratic wavenumber dependence becomes significant only when the correlation length begins to grow and $\xi \geq 2$.

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