

Facilitation, complexity growth, mode coupling, and activated dynamics in supercooled liquids

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Contributed by Peter G. Wolynes, September 4, 2008 (received for review, August 5, 2008)

In low-temperature-supercooled liquids, below the ideal mode-coupling theory transition temperature, hopping and continuous diffusion are seen to coexist. Here, we present a theory that shows explicitly the interplay between the two processes and shows that activated hopping facilitates continuous diffusion in the otherwise frozen liquid. Several universal features arise from nonlinear interactions between the continuous diffusive dynamics [described here by the mode coupling theory (MCT)] and the activated hopping (described here by the random first-order transition theory). We apply the theory to a specific system, Salol, to show that the theory correctly predicts the temperature dependence of the nonexponential stretching parameter, β , and the primary α relaxation timescale, τ . The study explains why, even below the mean field ergodic to nonergodic transition, the dynamics is well described by MCT. The nonlinear coupling between the two dynamical processes modifies the relaxation behavior of the structural relaxation from what would be predicted by a theory with a complete static Gaussian barrier distribution in a manner that may be described as a facilitation effect. Furthermore, the theory correctly predicts the observed variation of the stretching exponent β with the fragility parameter, D . These two predictions also allow the complexity growth to be predicted, in good agreement with the results of Capaccioli *et al.* [Capaccioli S, Ruocco G, Zamponi F (2008) *J Phys Chem B* 112:10652-10658].

complexity | glass transition | random first order

The glass transition is characterized by a number of interesting kinetic phenomena. Very slow and simultaneously nonexponential relaxation of time correlation functions over large time windows is one such important phenomenon. This relaxation is often approximated by the stretched exponential, Kohlrausch-William-Watts (KWW) formula, $\phi(t) = \exp(-(t/\tau)^\beta)$, with both β and τ exhibiting nontrivial temperature dependence. The origin of the stretching is usually attributed to the presence of dynamic heterogeneity in the system (1, 2). The temperature dependence of the typical relaxation time can be described by the Vogel-Fulcher-Tamman (VFT) expression, $\tau = \tau_{\text{VFT}} \exp(DT_o/(T-T_o))$, where τ_{VFT} is the high-temperature relaxation time, T_o is the VFT temperature, and D is the fragility index. The fragility index, D , determines the degree of deviation from the Arrhenius law that is appropriate for simple activated events. Experimental and theoretical model studies have shown that β and D are correlated (3-5). The temperature dependence of τ has also been described by phenomenological mode coupling theory (MCT) expression, $\tau \sim [(T - T_c^{\text{fit}})/T_c^{\text{fit}}]^{-\gamma}$, ($\gamma > 0$), but this ultimately breaks down at low temperature. T_c^{fit} is referred to as the MCT transition temperature. Above T_c^{fit} , MCT is found to explain many experimental results (6-9), and below T_c^{fit} , the MCT picture of continuous diffusion fails eventually. It is conjectured that this breakdown is due to the ergodic to nonergodic transition in the dynamics and below T_c^{fit} activated dynamics becomes a dominant mode of transport. However in an elegant work, Brumer and Reichman (10) (BR) have recently shown that the idealized MCT using microscopic input breaks down at a much higher temperature, T_c^0 , which corresponds to the temperature, T_L , where the landscape properties show

a sharp change. Kob *et al.* (11) have shown that the structural MCT predicts the proper dynamics till very close to T_c^{fit} but needs static inputs to be calculated at a higher effective temperature. Stevenson *et al.* (12, 13) have shown that below the ergodic to nonergodic transition but before the predicted crossover to the activated dynamics, string or fractal excitations drive the dynamics and that this qualitatively describes the crossover temperature as occurring at a specific value of the configurational entropy.

Computer simulation studies seem to show the coexistence of continuous diffusion and hopping as mechanism of mass transport at temperatures much above T_c^{fit} (14-17). These studies show that individual hopping events are often followed by enhanced continuous diffusion or more hops of the surrounding atoms or molecules (14, 15, 18). Simulations have also shown that a single hopping event relaxes the local stress (16), hence, it is expected that hopping events are followed by continuous diffusive dynamics. From BR study we know the temperature at which the ergodic to nonergodic transition takes place ($T_c^0 = T_L$) (10). However, there is no clear theoretical understanding of the dynamics in the range, $T_c^{\text{fit}} < T < T_c^0$. Furthermore, we need to understand, why, below T_c^0 , the MCT still seems to explain the form of the dynamics rather well and, finally, what happens at T_c^{fit} that leads to the breakdown of the MCT as far as the temperature dependence is concerned. In an earlier work it was shown that the full dynamics is a synergetic effect of continuous diffusive motion and activated dynamics (19). Here, we show how the coupling between these two dynamical processes influences each other. The coupling leads to hopping-induced diffusive motion below T_c^0 and thus explains the validity of MCT below T_c^0 . The study also explains the origin of the apparent breakdown of MCT at T_c^{fit} . The crucial result of the present study is that the coupling renormalizes the distribution of hopping barriers which participates in the dynamics. This provides a formal treatment of the facilitation effect discussed by Xia and Wolynes (4, 5) in their theory of the stretching exponent.

The present work uses a scheme of calculation similar to the one presented earlier (19) with a few modifications. For describing the diffusive motion we use the schematic F_{12} model of the MCT (20-22) but the activated hopping dynamics now have a static barrier height distribution (4, 5). The equation of motion for the total intermediate scattering function is written as,

$$\phi(t) \simeq \phi_{\text{MCT}}(t)\phi_{\text{hop}}^{\text{static}}(t). \quad [1]$$

In describing the activated dynamics we consider that there is a distribution of the hopping barriers in the system arising from the entropy fluctuation (4, 5). Thus, the total contribution from the

Author contributions: S.B., B.B., and P.G.W. designed research; S.B., B.B., and P.G.W. performed research; S.B., B.B., and P.G.W. contributed new reagents/analytic tools; S.B., B.B., and P.G.W. analyzed data; and S.B., B.B., and P.G.W. wrote the paper.

The authors declare no conflict of interest.

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multiple-barrier hopping events is written as,

$$\begin{aligned}\phi_{\text{hop}}^{\text{static}}(t) &= \int \phi_{\text{hop}}^s(t) \mathcal{P}^{\text{static}}(\Delta F) d\Delta F \\ &= \int e^{-tK_{\text{hop}}(\Delta F)} \mathcal{P}^{\text{static}}(\Delta F) d\Delta F,\end{aligned}\quad [2]$$

where $\mathcal{P}^{\text{static}}(\Delta F)$ is taken to be Gaussian,

$$\mathcal{P}^{\text{static}}(\Delta F) = \frac{1}{\sqrt{2\pi(\delta\Delta F)^2}} e^{-(\Delta F - \Delta F_o)/2(\delta\Delta F)^2}.\quad [3]$$

We call this distribution, the static barrier height distribution. Here, $\phi_{\text{hop}}^s(t) = e^{-tK_{\text{hop}}(\Delta F)}$ describes the activated hopping dynamics for a single hopping barrier. $K_{\text{hop}}(\Delta F) = \mathcal{F}(q)P_{\text{hop}}(\Delta F)$. The expression for $\mathcal{F}(q)$ is given by $\mathcal{F}(q) = \frac{v_0}{v_p}(1 - G(q))$.[¶] For the present work the q dependence of $\mathcal{F}(q)$ will be neglected and $\mathcal{F}(q)$ will be set to unity. $P_{\text{hop}}(\Delta F)$ is the average hopping rate, which is a function of the free-energy barrier height, ΔF , and is given by $P_{\text{hop}}(\Delta F) = \frac{1}{\tau_0} \exp(-\Delta F/k_B T)$ (23).

The equation of motion for the MCT part of the intermediate scattering function, $\phi_{\text{MCT}}(t)$, is written as,

$$\begin{aligned}\ddot{\phi}_{\text{MCT}}(t) + \gamma \dot{\phi}_{\text{MCT}}(t) + \Omega_0^2 \phi_{\text{MCT}}(t) \\ + \lambda_1 \Omega_0^2 \int_0^t dt' \phi_{\text{MCT}}(t') \phi_{\text{hop}}^{\text{static}}(t') \dot{\phi}_{\text{MCT}}(t - t') \\ + \lambda_2 \Omega_0^2 \int_0^t dt' [\phi_{\text{MCT}}(t') \phi_{\text{hop}}^{\text{static}}(t')]^2 \dot{\phi}_{\text{MCT}}(t - t') \\ = 0\end{aligned}\quad [4]$$

Now, the MCT part of the intermediate scattering function, $\phi_{\text{MCT}}(t)$ is self-consistently calculated with the full scattering function, $\phi(t)$. In describing the dynamics with schematic MCT the coupling between the different wave vectors is neglected and the contribution from the static and dynamic quantities is calculated at a single wavenumber $q = q_m$ (q_m is the wave number where the peak of the structure factor appears) which is known to provide the dominant contribution. In the present formalism it is assumed that hopping opens up multiple relaxation channels for the otherwise frozen MCT dynamics.

Eqs. 1 and 4 together describe the full dynamics, which is similar in spirit to the extended MCT (21) and other recent approaches (24). The similarity of the present scheme to the extended MCT of Gotze and Sjogren was elaborately analyzed in our earlier work (19).

As in our earlier work (19), the values of Ω_0 and γ are kept fixed at unity, neglecting their temperature dependence, and the scaling time is taken as 1 ps. $\lambda_1 = \frac{(2\lambda-1)}{\lambda^2} + \epsilon \frac{\lambda}{(1+(1-\lambda)^2)}$ and $\lambda_2 = \frac{1}{\lambda^2} + \epsilon \frac{\lambda(1-\lambda)}{(1+(1-\lambda)^2)}$ (21, 22). The MCT formalism predicts a relationship between λ and β_{MCT} as $\beta_{\text{MCT}} = -\log(2)/\log(1-\lambda)$ (22). ϵ is a measure of the distance from the ergodic to nonergodic transition temperature of the ideal MCT, T_c^0 , thus $\epsilon = \frac{T_c^0 - T}{T_c^0}$. To calculate the MCT part of the relaxation we need to estimate λ and T_c^0 . These quantities can be calculated for systems where the static quantities (like static structure factor) are known, but for realistic systems, because of the unavailability of the static quantities, the estimation becomes difficult. We thus use the following methods to estimate λ and T_c^0 . The ergodic to nonergodic transition is found to take place at T_L where the energy landscape properties first change (10), thus we set $T_c^0 = T_L$. T_L is also the

temperature where the stretching parameter starts falling (25). From experimental studies we know that for the Salol system the stretching parameter starts falling at $T = 278$ K (7). Thus, we estimate that $T_c^0 = T_L = 278$ K. Now, to estimate λ in this schematic MCT equation, we again make use of experimental results. MCT is expected to explain the dynamics above T_c^0 ; thus, the stretching parameter above T_c^0 should be equal to $\beta_{\text{MCT}} = 0.84$ (7). We have also mentioned that λ and β_{MCT} are related. Thus, λ is fixed in such a way that, above T_c^0 , we get the correct β_{MCT} .

Next, we discuss the hopping dynamics for the Salol system as predicted from random first-order transition (RFOT) theory. According to the RFOT theory, the free-energy cost, $F(r)$, which is used to calculate the mean barrier height, can be written as $F(r) = \frac{\Gamma_K(r)\Gamma_A(r)}{\Gamma_K(r)+\Gamma_A(r)} - \frac{4\pi}{3}r^3T_s c$, where $\Gamma_K(r)$ and $\Gamma_A(r)$ are the surface energy terms at T_K (Kauzmann temperature) and T_A (temperature where hopping barrier disappears), respectively (19, 23). The temperature dependence of the configurational entropy can also be given by an empirical formula (26), $s_c = s_{\text{fit}}(1 - T_K/T)$, where s_{fit} is a system dependent parameter which is also related to the specific heat jump at the Kauzmann temperature ($\Delta c_p(T) = s_{\text{fit}}(T_K/T)$). For the Salol system $s_{\text{fit}} = 2.65$, $T_K = 175$ K and $T_A = 333$ K. With these values of the parameters the mean barrier height and the critical nucleus radius are calculated. We find that at $T = 280$ K, the size of the critical nucleus is above unity. Thus, although $T_A = 333$ K, for all practical purposes $T = 280$ K should be considered as the temperature where activated events start, which, as found in simulations, is close to T_c^0 (17). The value of τ_0 is fixed in such a way that at $T = 280$ K, both the MCT and the hopping dynamics together predict a relaxation time that is close to that obtained in the experiment (8). Thus, for Salol the fitting gives $\tau_0 = 2400$ ps. A more microscopic treatment of the barrier height can be found by treating the shape of the nucleating region as a fuzzy sphere (12). The distribution of barrier heights arises due to the fluctuation in entropy density, which can be related to the specific heat according to the Landau formula, $\langle(\Delta S)^2\rangle = k_B C_p$ (27), where ΔS is the entropy fluctuation and C_p is the specific heat. This expression can be rewritten in terms of configurational entropy fluctuation per bead δs_c and heat capacity jump per bead $\Delta c_p(T)$ as, $\delta s_c = \sqrt{\frac{k_B \Delta c_p(T)}{\frac{4\pi}{3}(r^*/a)^3}}$ and $\frac{\delta s_c}{(s_c)} = \sqrt{\frac{3k_B T T_K}{4\pi s_{\text{fit}}(T - T_K)^2 (r^*/a)^3}}$. Here,

r^* is the droplet radius determined by using $F(r^*) = 0$. a is the length of the bead. We can also relate the entropy fluctuation to the width of the barrier height distribution, $\frac{\delta\Delta F}{\Delta F_o} \simeq \frac{\delta s_c}{1 + \frac{\delta s_c}{(s_c)}}$, and thus

define the width of the static barrier height distribution in terms of entropy fluctuation and specific heat.

Combining the static RFOT and MCT, we solve Eqs. 1 and 4 numerically.[¶] We use a numerical method presented earlier (28) with a minor modification (29). The total relaxation time, τ_{total} , and the stretching parameter, β_{total} , are obtained from the coupled dynamics by fitting the long time part of $\phi(t)$ (obtained from Eq. 1) to a KWW stretched exponential function, $\phi(t) = A \exp(-(t/\tau_{\text{total}}))^{\beta_{\text{total}}}$. Similarly from $\phi_{\text{MCT}}(t)$ we obtain the MCT relaxation time, τ_{MCT} , and the corresponding stretching parameter, β_{MCT} .

Hopping-Induced Continuous Diffusion

The plot for the relaxation time τ_{total} is given in Fig. 1, where we have also shown the experimental results (for Salol) and the fit to the MCT phenomenological expression. Already the temperature dependence of τ_{total} reveals several interesting physics. The τ_{total} compares well with the experimental results (8) and predicts the correct glass transition temperature, $T_g = 220$ K. Recall that in

[¶]In the previous article (19) there was a mistake in the derivation of the hopping kernel. The correct expression is presented here.

[¶]The results converge properly for the total time step $N = 510$ and the initial timestep for the integration is taken to be 10^{-9} ps.

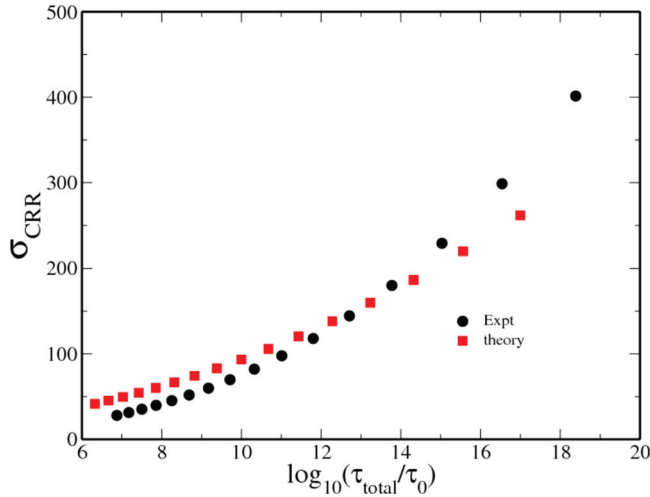


Fig. 5. Relation between alpha relaxation timescale and complexity of dynamically reconfiguring regions. σ_{CRR} calculated from the present theory (see footnote $\ddagger\ddagger$) (red squares) is plotted against $\log_{10}(\tau_{\text{total}}/\tau_0)$ for Salol by using the analysis of Capaccioli *et al.* (31). This τ_0 is the relaxation time at high temperature and different from the τ_0 used to describe the activated dynamics. We also plot the results presented by Capaccioli *et al.* (31) that they obtained from experimental data (black circles).

height distribution. Note that Xia and Wolynes (4) showed that the static barrier height distribution should have a cutoff to describe the relationship between β and D . The authors gave a physical explanation of this “cutoff” by using the picture of dynamic mosaic structure.

The combination of distributed activated hopping and mode coupling facilitation also explains some recent exciting experimental observations of Capaccioli *et al.* (31). These authors recognized that, in those theories of glassy dynamics based on an underlying entropy crisis, the complexity of a dynamically correlated region is a key quantity. They also used earlier insights (32, 33) to show how this quantity can be roughly inferred from experiment. This inference is independent of chemical details, such as bead count, which have previously been used for comparisons of RFOT theory with experiment.

The complexity, σ_{CRR} (the logarithm of the number of accessible states in a cooperatively rearranging region) is obtained by combining the configurational entropy density, S_c , inferred from calorimetry, with the temperature dependence of dynamics as reflected in the alpha relaxation time, $\tau_\alpha(T)$, and stretching exponent of dielectric relaxation or viscosity, $\beta(T)$ (31).

$$\sigma_{\text{CRR}}(T) = \frac{S_c}{\Delta C_p} \frac{\beta(T)}{e^2} \left(\frac{d \ln \tau_\alpha}{d \ln T} \right)^2 \quad [6]$$

In those purely kinetic models of the glass transition that are based on the facilitation concept but have trivial underlying thermodynamics (34), one would not expect this inferred complexity to be a universal function of the relaxation time. However, according to the Adam–Gibbs argument, the complexity should be a constant for all values of the relaxation time but could depend on substance. The static RFOT theory predicts that the logarithm of the relaxation timescales should be a universal function of the complexity of the dynamically reconfiguring regions for all glass formers. In contrast to the expectations from thermodynamically trivial kinetic models, Capaccioli *et al.* (31) showed a very strong data collapse of this complexity, σ_{CRR} versus $\log_{10}(\tau_\alpha)$ for many substances. The Adam–Gibbs prediction of a constant value is not borne out, however. In contrast also to static RFOT, which predicts an asymptotically linear relation, the experimental data show a distinct curvature.

In Fig. 5 we show the prediction of σ_{CRR} versus $\log_{10}(\tau_{\text{total}}/\tau_0)$ that is obtained from the present calculation $\ddagger\ddagger$ for Salol using the analysis of Capaccioli *et al.* along with their results (31). In harmony with the experimental observation we see that the combined MCT/activated RFOT mechanism does give a curvature. The universal curve obtained experimentally was fit by an assumed scaling form containing several adjustable exponents. The present calculations suggest that the true asymptotic region may not yet have been reached experimentally. At the same time, we must be clear that the present calculation is still a low-order one. It is conceivable that a renormalization group treatment, in which the static RFOT barriers themselves are modified by the MCT effects that occur on shorter-length scales, could ultimately give anomalous scaling even in the ultimate asymptotic regime.

The present study enriches our understanding of the dynamics below the ergodic to nonergodic transition temperature, T_c^0 . It predicts the presence of hopping-induced diffusive dynamics below T_c^0 . It also predicts that this diffusive dynamics continues to exist even below T_c^{fit} and provides a dominant contribution to the total dynamics. However, in this temperature range there is an increased contribution from the activated dynamics that leads to the breakdown of the MCT. The diffusive dynamics is found to modify the activated dynamics by redefining the barrier height distribution of the hopping events in a way such that the higher barriers are excluded from the total dynamics. Thus, we find that in this unified theory the two dynamical processes do not just act as parallel channels of relaxation, but they interact with each other and modify each other’s behavior, which leads to the facilitation of the total dynamics.

Materials and Methods

Relationship Between τ_{total} and ΔF . According to the present theory, $\tau_{\text{total}} = \frac{1}{K_{\text{MCT}} + K_{\text{hop}}}$, where $K_{\text{hop}} = \frac{1}{\tau_0} \exp(-\Delta F/k_B T)$. Even for the simple exponential MCT relaxation the relationship between K_{MCT} and ΔF is nontrivial (29).

However, in the low-temperature limit we can write $K_{\text{MCT}} = \frac{2K_{\text{hop}}}{\lambda_2 A^2 + 2\lambda_1 A - 1} = \alpha K_{\text{hop}}$, where $\alpha = \frac{2}{\lambda_2 A^2 + 2\lambda_1 A - 1}$. A is the Debye–Waller factor or the form

factor (height of the plateau), thus, $\tau_{\text{total}} = \frac{1}{(\alpha + 1)K_{\text{hop}}} \cdot \Delta F_0$, is calculated at $T = T_g$, by using Salol parameters. $\delta \Delta F$ is related to $\beta_{\text{hop}}^{\text{static}}$ [by $\beta_{\text{hop}}^{\text{static}} = [1 + (\delta \Delta F/k_B T)^2]^{-1/2}$ (4, 30)] and it is taken in such a way that it gives $\beta_{\text{hop}}^{\text{static}} = 0.5$. We calculate the total relaxation and fit it to a stretched exponential. From the fitting we obtain τ_{total} and β_{total} . This is now fed into Eq. 5 to obtain $\mathcal{P}^{\text{dynamic}}(\Delta F)$.

Fragility Dependence of β_{total} . The mean barrier height depends on the configurational entropy and is almost independent of the system; thus, for all the systems (12), we calculate ΔF_0 by using Salol parameters ($S_{\text{fit}} = 2.65$, $T_K = 175$ K, $T_c^0 = 278$ K). $\delta \Delta F$ is fixed according to the value of D , which is taken from Bohmer *et al.* (3). For the Salol system τ_0 is used as a fitting parameter to describe the proper timescale of the dynamics. In this calculation we also vary τ_0 for each system in such a way that at $T = T_g$ the relaxation time is of the order of 100 s. We find that, for a more fragile system, we need a larger value of τ_0 .

Above T_c^{fit} , the dynamics is expected to be described completely by the MCT. Thus, the β_{total} above T_c^0 should be equal to the β_{MCT} value. For the systems like Salol (6), Glycerol (35), and Silica [Silica is known to be a strong liquid with $\beta \simeq 1$] where the value of β_{expt} at high temperatures is known, we use these values to define β_{MCT} . For the systems where β_{expt} at high temperatures are not known, we use a reasonable value [definitely larger than $\beta_{\text{expt}}(T = T_g)$] and also vary it in small amounts along with τ_0 to get the proper relaxation timescale at T_g . T_c^0 is kept same as that for the Salol system. So, our only constraint is that the timescale should be of the order of 100s at T_g .

ACKNOWLEDGMENTS. S.M.B. thanks Prof. K. Miyazaki for discussions. This work was supported in part by Department of Science and Technology, J.C. Bose Fellowship, and the National Science Foundation.

$\ddagger\ddagger$ σ_{CRR} is calculated from Eq. 6. In the calculation, the temperature dependence of S_c and ΔC_p are calculated by using the empirical forms (for details, see text) (26). The temperature dependence of τ_{total} is obtained from the theory (Fig. 1). In our theory, although we predict a temperature dependence of $\beta(T)$, to compare our results with Capaccioli *et al.* (31) we have considered, following those authors, $\beta(T)$ to be independent of T . We fixed it to its value at $T = T_g$. For this plot we take $\tau_0 = 10^{-3.9}$ ps (31).

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