Hopping induced continuous diffusive dynamics below the non-ergodic transition

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In low temperature supercooled liquid, below the ideal mode coupling theory transition temperature, hopping and continuous diffusion are seen to coexist. We present a theory which incorporates interaction between the two processes and shows that hopping can induce 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 real systems (Salol) to show that the theory correctly predicts the temperature dependence of the non-exponential stretching parameter, \( \beta \), and the primary relaxation timescale, \( \tau \). The study explains why, even below the ergodic to non-ergodic transition, the dynamics is well described by MCT. The non-linear 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 explains the observed variation of the stretching exponent \( \beta \) with the fragility parameter, \( D \).

I. INTRODUCTION

The glass transition is characterized by a number of interesting kinetic phenomena. Slow non-exponential relaxation of time correlation functions over large time windows is one such important phenomenon. This relaxation is usually well approximated by the stretched exponential, Kohlrausch-William-Watts (KWW) formula \([1] \), \( \phi(t) = \exp(-(t/\tau)^\beta) \), with both \( \beta \) and \( \tau \) exhibiting non trivial temperature dependence. The origin of the stretching is usually attributed to the presence of dynamic heterogeneity in the system \([2, 3] \). The temperature dependence of the relaxation time can be described by the Vogel-Fulcher-Tamman (VFT) expression, \( \tau = \tau_0 \exp(D_T/(T-T_0)) \), where \( \tau_0 \) is the high temperature relaxation time, \( T_0 \) is the VFT temperature and \( D \) is the fragility index. The fragility index, \( D \) determines the degree of deviation from the Arrhenius law. Experimental and theoretical model studies have shown that \( \beta \) and \( D \) are correlated \([4, 5] \). The temperature dependence of \( \tau \) is also described by phenomenological MCT expression, \( \tau \sim [(T-T_f^{\text{fit}})/T_f^{\text{fit}}]^{-\gamma} \), \( \beta \) (\( \gamma > 0 \)). \( T_f^{\text{fit}} \) is referred to as the MCT transition temperature. Above \( T_f^{\text{fit}} \), MCT is found to explain many experimental results \([6, 7, 8, 9, 10] \), and below \( T_f^{\text{fit}} \), the MCT description of continuous diffusion breaks down. It is conjectured that this breakdown is due to the ergodic to non-ergodic transition in the dynamics and below \( T_f^{\text{fit}} \) activated dynamics becomes a dominant mode of transport. However in an elegant work, Burmer and Reichman \([11] \) (BR) have recently shown that the idealized MCT breaks down at a much higher temperature, \( T_0 \), which corresponds to the temperature, \( T_L \), where the landscape properties change. Kob et al. have shown that the structural MCT predicts the proper dynamics till very close to \( T_f^{\text{fit}} \) but needs static inputs to be calculated at a higher effective temperature \([12] \). Wolynes and co-workers have shown that below the ergodic to non-ergodic transition but before the predicted crossover to the activated dynamics, string or fractal excitations drive the dynamics \([13] \).

Computer simulation studies predict the coexistence of continuous diffusion and hopping as mechanism of mass transport at temperatures much above \( T_f^{\text{fit}} \) \([14, 15] \). These studies show that individual hopping events are often followed by enhanced continuous diffusion or more hops of the surrounding atoms or molecules \([14, 16] \). Simulations have also shown that a single hopping event relaxes the local stress \([14] \), hence it is expected that hopping events are followed by continuous diffusive dynamics. As mentioned earlier, from BR study we know the temperature where the ergodic to non-ergodic transition takes place \( T_0 = T_L \) \([11] \). However, there is no clear theoretical understanding of the dynamics in the range, \( T_f^{\text{fit}} < T < T_0 \). Furthermore, we need to understand, why below \( T_0 \) the MCT still seems to explain the dynamics rather well and finally, what happens at \( T_f^{\text{fit}} \) that leads to the breakdown of the MCT.

In an earlier work it was shown that indeed below the ergodic to non-ergodic transition, both activated and continuous diffusion mechanisms are present. These two are nonlinearly coupled and may drive each other \([17] \). It was shown that the full dynamics is a synergetic effect of continuous diffusive motion and activated dynamics \([17] \).

Here we show that the above coupling can lead to quite interesting phenomena. First for the Salol system we find that, the theory predicts the correct temperature dependence of relaxation time. Following BR analysis \([11] \) we consider that the ergodic to non-ergodic transition in the
ideal MCT occurs at $T_c^0 = 278k$. However, when we fit the relaxation timescale to the phenomenological MCT expression, the timescale shows an apparent divergence at a lower temperature, thus predicting $T_c^{fit} = 258K$ which is similar to that found in experimental studies. Thus the study demonstrates that well below the idealized MCT ergodic to non-ergodic transition temperature where non-mean field activated events are present, the dynamics can be well described by MCT. We find that, across $T_c^{fit}$, although both the transport mechanisms are operative and there is no discontinuity in their motion, there is an abrupt or sudden rise in the contribution from the activated events. This leads to the apparent breakdown of the MCT.

Second, the theory predicts the correct temperature dependence of the stretching parameter $\beta$. We find that the bare barrier height distribution that describes isolated hopping, gets renormalized due to the coupling of the hopping dynamics to the continuous diffusive motion. The renormalized distribution of the barriers, referred to as the dynamic barrier height distribution, is different from the initial assumption of distribution referred to as the static barrier height distribution. There is a preference for low barrier hopping events leading to facilitation effect. Third, due to facilitation effect, the theory predicts a correct relationship between the stretching parameter, $\beta$, and the fragility index, $D$.

The organization of the rest of the paper is as follows. In the next section we describe the theoretical scheme. Section 3 contains results and discussions. Section 4 concludes with a discussion on the results.

II. THEORETICAL FORMULATION

The present work uses a scheme of calculation similar to the one presented earlier [17] with a few modifications. For describing the diffusive motion we use $F_{12}$ model of the MCT [18] and we also describe the activated hopping dynamics with a static barrier height distribution [5]. In describing the dynamics the coupling between the different wave-vectors are neglected and the contribution from the static and dynamic quantities are calculated at a single wavenumber $\mathbf{q} = q_m$ ($q_m$ is the wave number where the peak of the structure factor appears) which is known to provide the dominant contribution. The MCT part of the intermediate scattering function, $\phi_{MCT}(t)$ is self consistently calculated with the full scattering function, $\phi(t)$. In writing the equation of motion we consider that there are distribution of hopping barriers in the system arising from the entropy fluctuation [5]. We know that in the absence of hopping motion the MCT dynamics below certain temperature is completely frozen, leading to a separation of time scale between the hopping dynamics and MCT dynamics. Thus for the frozen MCT dynamics, it appears that multiple relaxation channels (present due to different hopping barriers) open up and all these channels act in parallel to relax the system. Thus when the contribution from these multiple hopping are included in the total relaxation, the equation of motion of MCT part of the intermediate structure function, $\phi_{MCT}(t)$, can be written as,

$$\dot{\phi}_{MCT}(t) + \gamma \phi_{MCT}(t) + \Omega_o^2 \phi_{MCT}(t)$$

$$+ \lambda_1 \Omega_o^2 \int_0^t dt' \phi_{MCT}(t') \sum \phi_{hop}(t') \phi_{MCT}(t-t')$$

$$+ \lambda_2 \Omega_o^2 \int_0^t dt' \phi_{MCT}(t') \sum \phi_{hop}(t')^2 \phi_{MCT}(t-t')$$

$$= 0 \quad (1)$$

Eq.(1) is essentially of the same general form as derived by Sjogren and Gotze for the extended mode coupling theory [19]. This point has been elaborately analyzed in an earlier work [17]. In deriving equation (1) we consider that the total intermediate scattering function is written as,

$$\phi(t) \approx \phi_{MCT}(t) \sum \phi_{hop}(t). \quad (2)$$

Here $\phi_{hop}(t) = \frac{1}{s+K_{hop}(q,\Delta F)}$ describes the activated hopping dynamics for a single hopping barrier. $K_{hop}(q,\Delta F) = F(q)P_{hop}(\Delta F)$. The expression for $F(q)$ is given by, $F(q) = \frac{\pi q^2}{\nu^2}(1 - G(q))$. For the present work the $q$ dependence of $F(q)$ will be neglected and $F(q)$ will be set to unity. $P_{hop}(\Delta F)$ is the average hopping rate which is a function of the free energy barrier height, $\Delta F$ and is given by $P_{hop}(\Delta F) = \frac{1}{\tau_0} \exp(-\Delta F/k_BT)$ [20]. The total contribution from multiple barrier hopping motion is written as, $\sum \phi_{hop}(t) = \int \phi_{hop}(t) P_{static}(\Delta F) d\Delta F = \int e^{-tK_{hop}(\Delta F)} P_{static}(\Delta F) d\Delta F$ where $P_{static}(\Delta F)$ is considered to be Gaussian, $P_{static}(\Delta F) = \frac{1}{\sqrt{2\pi}\Delta F} \exp(-\Delta F^2/2\Delta F^2)$. We will call this distribution as the static barrier height distribution.

We now discuss the MCT part of the calculation. As in our earlier model calculation [17], the values of $\Omega_o$ and $\gamma$ are kept fixed at unity, neglecting their temperature dependence and the scaling time is taken as $1ps$. $\lambda_1 = \frac{(2\lambda-1)}{\lambda} + \lambda$ and $\lambda_2 = \frac{1}{\nu^2} + \frac{1}{\nu^2}$. The MCT formalism predicts a relationship between $\lambda$ and $\beta_{MCT}$ as $\beta_{MCT} = -log(2)/log(1-\lambda)$. $\epsilon$ is a measure of the distance from the ergodic to non-ergodic transition temperature of the ideal MCT, $T^{0}_C$, thus $\epsilon = \frac{T^{0}_C - T}{T^{0}_C}$. Thus to calculate the MCT part of the relaxation we need to estimate $\lambda$ and $T^{0}_C$. These quantities can be calculated for systems where the static quantities (like static structure factor) are known, but for realistic system due to the unavailability of the static quantities the estimation becomes difficult. We thus use the following methods to estimate $\lambda$ and $T^{0}_C$. According to the analysis of BR, the ergodic to non-ergodic transition takes place at the temperature, $T_L$ where the energy landscape properties first change [11], thus $T^{0}_C = T_L$. According to Sastri et al [22], $T_L$ also coincides with the temperature where the stretching parameter starts falling. From experimental studies
we know that for Salol system the stretching parameter starts falling at \( T = 278K \) [7]. Thus we estimate that \( T^0_\lambda = T_\lambda = 278K \). Now for the estimation of \( \lambda \) we again make use of experimental results. MCT is expected to explain the dynamics above \( T^0_\lambda \), thus the stretching parameter above \( T^0_\lambda \) should be equal to \( \beta_{\text{MCT}} = 0.84 \) [3]. We have also mentioned that \( \lambda \) and \( \beta_{\text{MCT}} \) are related. Thus \( \lambda \) is fixed in such a way that, above \( T^0_c \), we get the correct \( \beta_{\text{MCT}} \).

Next we discuss the implementation of the hopping dynamics for Salol system using the predictions of random first order transition (RFOT) theory. According to the RFOT theory, the mean barrier, \( F(r) \), which is used to calculate the mean barrier height, can be written as \( F(r) = \frac{\Gamma_K(r)\Gamma_A(r)}{\Gamma_K(r)+\Gamma_A(r)} - \frac{4\pi}{3}e^3T_s c \) 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 [17, 21]. The temperature dependence of the configurational entropy can also be given by an empirical formula, [23] \( s_c = s_{\text{fit}}(1 - T_K/T) \) where \( s_{\text{fit}} \) 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 \( s_{\text{fit}} = 2.65, T_K = 175K \) and \( T_A = 333K \). With these values of the parameters the mean barrier height and the critical nucleus radius are calculated. We find that at \( T = 280K \), the size of the critical nucleus is above unity. Thus although \( T_A = 333K \), for all practical purpose \( T = 280K \) should be considered as the temperature where activated events start. Note that as found in simulations [15] this temperature is close to \( T^0_\lambda \). The value of \( \tau_0 \) is fixed in such a way that at \( T = 280K \), both the MCT and the hopping dynamics together predict a relaxation time which is close to that obtained in the experiments [3]. Thus for Salol system we find \( \tau_0 = 2400ps \). The barrier height can also be calculated by considering the shape of the nucleating region to be a fuzzy sphere [13]. The distribution of barrier height arises due to the fluctuation in entropy which can be related to the specific heat according to the Landau formula, \( \langle \Delta S \rangle^2 \approx k_B C_p \) [24] where \( \Delta S \) is the entropy fluctuation and \( C_p \) is the specific heat. This expression can be rewritten in terms of configurational entropy fluctuation per bead \( \delta s_c \) and heat capacity jump per bead \( \Delta c_p(T) \) as,

\[
\delta s_c = \sqrt{\frac{k_B \Delta c_p(T)}{4 \pi s_{\text{fit}}(T_K/T)}} \quad \text{and} \quad \delta s_{\text{sc}} = \sqrt{\frac{3k_B T_K}{4 \pi s_{\text{fit}}(1 - T_K/T)}}.
\]

Here \( r^* \) is the droplet radius determined 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, \( \Delta \Delta E_c \approx \frac{\delta s_{\text{sc}}}{1 + \frac{\delta s_{\text{sc}}}{\delta s_c}} \), and thus define the width of the static barrier height distribution in terms of entropy fluctuation and specific heat.

Note that from the main equations of motion (eq.1 and eq.2) it is obvious that the hopping dynamics interacts with the MCT dynamics and thus effects the MCT dynamical correlation. But, the effect of MCT dynamics on the hopping motion is not so obvious. However, we will show below that the interaction between \( \phi_{\text{MCT}} \) and \( \phi_{\text{hop}} \) generates a renormalized barrier height distribution that is explored by the system. A treatment consistent with this renormalized barrier height distribution has not been attempted, although results should not be too different from the ones presented here.

III. NUMERICAL RESULTS

We solve equations 1 and 2 numerically using a numerical method presented earlier [23] with a minor modification [20]. The essential idea involved in the method is to separate the slow and the fast variables and treat them differently in the convolution. The short time part of \( \phi(t) \) and \( \phi_{\text{MCT}}(t) \) are calculated exactly with very small step-size [27] and they are then used as input to carryout the calculation for the long time part of the same. The total relaxation time, \( \tau_{\text{total}} \) and the stretching parameter, \( \beta_{\text{total}} \) is obtained from the coupled dynamics by fitting the long time part of \( \phi(t) \) (obtained from eq.2) to a KWW stretched exponential function, \( \phi(t) = A \exp((-t/\tau_{\text{total}})^{\beta_{\text{total}}}) \).

The plot for the relaxation time \( \tau_{\text{total}} \) is given in Fig.1 where we have also shown the experimental results (for Salol) and the fit to the MCT phenomenological ex-

![FIG. 1: Temperature dependence of the time scale of longtime α relaxation for Salol. The timescale for the longtime part of the total structural relaxation, \( \phi(t) \), obtained from experiments [3] (black circles) and that calculated from the present coupled theory, \( \tau_{\text{total}} \) (red diamonds) are plotted against temperature. We fit the \( \tau_{\text{total}} \) to the MCT phenomenological expression, \( \tau_{\text{total}} \sim (T - T^0_{\lambda})/\gamma_{\text{MCT}} \) (blue dashed line), we obtain \( T^0_{\lambda} = 258K \). In inset we plot \( \left( \tau_{\text{MCT}} - \tau_{\text{total}} \right)/\tau_{\text{total}} \) as obtained from the theory (red stars). The black dashed line is a guide to the eye. The function shows a jump around \( T = 258K \). We find that across this temperature the hopping dynamics changes its role and below \( T^0_{\lambda} = 258K \) it plays a "direct" role in the dynamics.
expression. As evident from the figure, the temperature dependence of $\tau_{total}$ reveals several interesting physics. The $\tau_{total}$ compares well with the experimental results $^8$ and predicts the correct glass transition temperature, $T_g = 220K$. Recall that in our calculation the ergodic to non-ergodic transition takes place at $T^0_c = 278K$ where the activated dynamics also becomes significant. Thus we know that the idealized MCT prediction breaks down at $T = 278K$ and below this temperature, its validity as such is unclear. However when we fit the relaxation time to MCT expression ($\tau \sim [(T - T^{fit})/T^{fit}]^{-\gamma}$) we obtain a value, $T^{fit}_c = 258K$, which is in excellent agreement with the experimental studies $^6, 9, 10$.

The advantage of the present scheme of calculation is that although it addresses the coupling between the continuous diffusion and the hopping motion, one can separately analyze their relative contributions to the total dynamics and explore the origin of the apparent validity of the MCT below $T^0_c$. Due to the nonlinear coupling in Eqs.1 and 2 the activated dynamics plays both a "direct" and a "hidden" role in the total relaxation. The "direct" role is the direct relaxation of $\phi$ via $\phi_{hop}$. However, if we analyze the structure of Eq.1 we find that the role of activated dynamics is also to soften the growth of the longitudinal viscosity which finally leads to the relaxation of the otherwise frozen $\phi_{MCT}$. Thus $\phi_{hop}$ plays a "hidden" role in the relaxation by helping $\phi_{MCT}$ to relax. We now analyze these two different roles of the hopping dynamics and their effect on the total relaxation.

Our study shows that both continuous dynamics and activated dynamics changes continuously across $T^{fit}_c$. However, when we plot $(\tau_{MCT} - \tau_{total})/\tau_{total}$ against $T$ (in the inset of Fig. 1) we find that this quantity undergoes a jump like increase in the temperature range of the phenomenological MCT transition temperature $T^{fit}_c$. This implies that although below $T^{fit}_c$ the continuous diffusion still remains as the dominant mode of relaxation, there is a change of role and increased contribution of the activated dynamics. The plot suggest that in the range, $T^{fit}_c < T < T^0_c$, the activated dynamics plays only a "hidden" role whereas below $T^{fit}_c$ it also plays a "direct" role in the relaxation process.

Thus in the range, $T^{fit}_c < T < T^0_c$, the role of the activated dynamics is primarily to open up the bottle neck to start the diffusive dynamics. Once the latter starts, the relaxation primarily takes place via the diffusive channel and all the MCT predictions hold good. This provides a quantitative explanation of the observations reported by Kob et al. $^{12}$. The authors find that till close to $T^{fit}_c$ the dynamics can be described via MCT although needs the static inputs to be calculated at a higher effective temperature.

Figure 1 shows the important result that although idealized MCT breaks down at $T^0_c = 278K$, the functional form of MCT continues to describe the dynamical characteristics till 258K. The latter is a widely known result, usually obtained from fitting the MCT functional forms to the experimental data $^6, 9, 10$. Thus our study provides an explanation of this intriguing result in terms of the interaction between the MCT and activated dynamics which leads to hopping induced continuous diffusive motion. The study further predicts that below $T^{fit}_c$ although the continuous diffusive dynamics plays an important role in the relaxation, the increased contribution from the activated dynamics finally leads to the breakdown of the MCT predictions.

In Fig.2 we plot the calculated temperature dependence of the stretching parameter $\beta$. In the same figure we also plot $\beta$ as predicted by the MCT and the RFOT theory (using static barrier height distribution) and also the experimental results on Salol $^4, 7$. It is clear that neither the MCT nor the RFOT can alone describe the proper temperature dependence of the stretching parameter. However, the coupled theory predicts a temperature dependence of $\beta_{total}$ which is qualitatively similar to that found in experiments. The stretching parameter is known to provide a measure of the heterogeneity and the system. In our study the heterogeneity arises from the distribution of hopping barriers. However, below $T^0_c$, $\beta_{total}$ is smaller than $\beta_{RFOT}$ which means that the barrier height distribution which participates in the dynamics (dynamic barrier height distribution) is narrower than the initial assumption of distribution (static barrier height distribution). This modification of the barrier height distribution (or heterogeneity) takes place due to the coupling between the diffusive and activated dynamics. The timescale analysis reveals that the smaller
barriers contribute to the dynamics, which implies that the coupling leads to the facilitation effect. The proper temperature dependence of $\beta_{\text{total}}$ implies that the theory correctly predicts the modified barrier height distribution and thus the growth in dynamic heterogeneity.

To quantify these points, we carry out the following analysis. Nonexponential relaxation in the system can be considered as arising from superposition of exponentials,

$$e^{-(t/\tau_{KW})^\beta_{KW}} = \int_0^\infty e^{-t/\tau} p_{\text{dynamic}}(\tau) d\tau$$

(3)

It is now possible to find the distribution function of the relaxation times $p_{\text{dynamic}}(\tau)$ by Laplace inverting the stretched exponential. Note that it is only possible to find $p_{\text{dynamic}}(\tau)$ when the individual dynamics is exponential. Hence we do this analysis of the distribution of relaxation times (and thus the barrier heights which participate in the dynamics) considering only exponential MCT relaxation. Once we obtain the distribution of relaxation times we can convert it into the distribution of barrier heights using, $p_{\text{dynamic}}(\Delta F) d\Delta F = p_{\text{dynamic}}(\tau) d\tau$, provided $\tau$ can be expressed in terms of $\Delta F$. The details are presented in the Appendix A. We now analyze the dependence of $p_{\text{dynamic}}(\Delta F)$ on the MCT relaxation time and show that $p_{\text{dynamic}}(\Delta F)$ not only depends on $p_{\text{static}}(\Delta F)$ but also depends on the MCT relaxation time $\tau_{MCT} = K_{MCT}^{-1}$. We fix the $p_{\text{static}}(\Delta F)$ and change the $\tau_{MCT}$ by calculating the MCT dynamics (which is coupled to $p_{\text{static}}(\Delta F)$) at different temperatures. The results are presented in Fig.3

At high temperatures, where MCT dynamics is fast, $p_{\text{dynamic}}(\Delta F)$ is narrow ($\beta_{KW}$ is large), and the position of the maximum, $\Delta F_{\text{max}}$, is shifted to smaller $\Delta F$ (Fig.3). We also find that as the MCT dynamics slows down, the distribution becomes broader and more non-Gaussian ($\beta_{KW}$ also becomes smaller), larger barriers contribute to the dynamics, and $\Delta F_{\text{max}}$ shifts to higher values (though it always remains smaller than $\Delta F_0$).

These findings are in accord with the literature. We know that as the temperature is lowered (or the dynamics becomes slower) there is a growth in dynamic heterogeneity. Thus we may say that $p_{\text{dynamic}}(\Delta F)$ provides a mean field estimation of the dynamic heterogeneity. Note that $p_{\text{dynamic}}(\Delta F)$ is always narrower than $p_{\text{static}}(\Delta F)$ and overlaps with it only in the low barrier side. Xia and Wolynes have given a physical interpretation of this exclusion of the higher barriers from the dynamics, using the picture of dynamic mosaic structure [5]. Since the exclusion of higher barriers fastens the hopping dynamics thus this is termed as “facilitation effect”. Our theoretical model does not explicitly consider these mosaic structures. However, we find that the presence of the continuous dynamics and its coupling to the activated dynamics leads to the facilitation effect. Note that the facilitation is strongest when the MCT dynamics is exponential and should be weaker when we have stretching in the MCT dynamics.

Next we show that this modification of the barrier
heights, as predicted by the present theory plays a key role in describing the proper relationship between the fragility index, $D$, and the stretching parameter, $\beta$. The study of Bohmer et al.\cite{bohmer} predicts a relationship between the fragility index $D$ and the stretching parameter $\beta$ at $T = T_g$. As discussed in Ref.\cite{burner}, $\beta_{\text{static}}$ is related to the width of the static Gaussian distribution of the barrier heights $\delta \Delta F$. $\delta \Delta F$ can be related to the fragility, $D$, as $\delta \Delta F \approx \frac{1}{2} \frac{\Delta f}{k_B T}$. Thus $\beta_{\text{hop}}$ can be related to the fragility $\beta = [1 + \left(\Delta F_{\text{hop}} / 2k_B T \sqrt{T/D}\right)^2]^{-1/2}$. However, it was found that this expression alone (with the full static barrier height distribution) does not describe the correct relationship between $\beta$ and $D$.\cite{burner}

The details of the calculation are presented in Appendix B. In Fig.\cite{burner} we plot the relationship between $\beta_{\text{total}}$ and $D$ as predicted by the present theory. In the same plot we also show the experimental results\cite{bohmer}. We find that the present theory captures the correct trend. This is to be contrasted with the predictions obtained from the static distribution of barrier heights. Note that in all the cases, $\beta_{\text{total}} > \beta_{\text{hop}}$, which implies that $P_{\text{dynamic}}(\Delta F)$ is always narrower than $P_{\text{static}}(\Delta F)$. Earlier we have shown that $P_{\text{dynamic}}(\Delta F)$ overlaps with $P_{\text{static}}(\Delta F)$ only on the low barrier side. Thus the higher barriers do not participate in the dynamics leading to facilitation effect. Hence, for a wide range of systems the theory predicts a proper modification of the barrier heights distribution. Note that it was shown by Xia and Wolynes that the static barriers height distribution needs a cut-off to describe the relationship between $\beta$ and $D$.\cite{burner}

The authors gave a physical explanation of this "cutoff" using the picture of dynamic mosaic structure.

IV. CONCLUDING REMARKS

In this article we present a theory that combines the effects of continuous dynamics (through mode coupling theory) and the activated dynamics (through random first order transition theory) in terms of a unified theory. In this unified theory the two dynamics do not just act as parallel channels of relaxation, but they interact with each other in a way that in the course of describing the dynamics they both modify each others behavior. Certain universal aspects of this work arise from this non-linear interactions. We show that the unified theory can provide satisfactory description of the relaxation over the whole temperature plane\cite{burner} and can explain the temperature dependence of the relaxation time, $\tau$ and the stretching parameter $\beta$. It also predicts the said relation between $\beta$ and $D$.

The difficulty of performing MCT calculations for realistic systems is the non-availability of the static quantities. This difficulty can be overcome if we can estimate the ergodic to non-ergodic transition temperature $T^*_c$. Following the analysis by Burner and Reichman,\cite{burner} we assume that the ergodic to non-ergodic transition takes place at the temperature where the landscape energy first starts changing, $T_L$, thus $T^*_c = T_L$. We next use the observations reported by Sastry et al that $T_L$ coincides with the emergence of non-exponential relaxation\cite{sastry}. From experimental studies we obtain $T^*_c = T_L = 278K$.\cite{burner} In accord with simulation studies\cite{burner} in the present theory, the activated dynamics becomes significant, close to $T^*_c$. Thus in our theory, below $T^*_c$, the MCT can only relax with the aid of the activated dynamics. In this theory, below $T^*_c$, the activated dynamics plays both a "hidden" and a "direct" role in the relaxation. The "direct" role is when it directly helps in structural relaxation and the "hidden" role is when it primarily lowers the longitudinal viscosity thus helping the otherwise frozen continuous diffusive dynamics to be active and help in the structural relaxation. The relaxation time $\tau_{\text{total}}$ obtained from the unified theory agrees well with experiments\cite{burner}. Although we consider the ergodic to non-ergodic transition and the activated dynamics to start at $T^*_c$, we find that when $\tau_{\text{total}}$ is fitted to MCT expression it shows a MCT transition temperature $T^{\text{fit}}_c = 258K$. We find that although the continuous and activated dynamics changes continuously across $T^{\text{fit}}_c$ the function $(T/MCT-\tau_{\text{total}})/\tau_{\text{total}}$ shows a jump across $T^{\text{fit}}_c$. This implies that hopping dynamics changes its role across $T^{\text{fit}}_c$. In the range $T^{\text{fit}}_c < T < T^*_c$, it primarily plays a "hidden" role and the dynamics is well described by the MCT. This explains the study of Kob et al.\cite{kob} and also the success of MCT in explaining experimental results below $T^*_c$.\cite{burner} However, below $T^{\text{fit}}_c$, there is a sudden increase in the contribution from the activated dynamics and it plays a "direct" role in the relaxation, which results in the breakdown of the MCT predictions. Our study predicts that below $T^{\text{fit}}_c$, even though the MCT breaks down, the continuous dynamics persists and plays an important role in the relaxation.

Note that in an earlier simulation study we have shown the coexistence of the continuous and activated dynamics and we have further shown that activated dynamics, which is usually followed by continuous diffusive dynamics, relaxes the local stress.\cite{burner} Thus the simulations studies have already observed the "hidden" role of hopping which has been predicted in the present study.

The theory can also predict the correct temperature dependence of the stretching parameter. Due to the growth of dynamic heterogeneity in the system the $\beta$ value is expected to decrease with $T$. While MCT does not predict any temperature dependence of the stretching parameter and RFOT theory predicts a strong temperature dependence of $\beta_{\text{hop}}$, the prediction of the present theory is closer to the experimental results. The $T$ dependence of the $\beta_{\text{total}}$ arises due to the barrier height distribution of the activate dynamics. However, we find that the barrier height distribution which participates in the dynamics $P_{\text{dynamic}}(\Delta F)$ gets modified from the static barrier height distribution, $P_{\text{static}}(\Delta F)$ which is used as an input. The coupling of the MCT dynamics with the activated dynamics is found to lead to this modification. The higher barriers in $P_{\text{static}}(\Delta F)$ are
not present in $P_{\text{dynamic}}(\Delta F)$, predicting a facilitation effect. We have shown that as the relaxation time of the system slows down, $P_{\text{dynamic}}(\Delta F)$ becomes broader and includes higher barriers. Thus we predict that $P_{\text{dynamic}}(\Delta F)$ provides a mean field estimation of the dynamic heterogeneity. We also find that this modification of the barrier height distribution, enables the theory to predict a proper relation between the fragility index $D$ and the stretching parameter, $\beta$.

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**Appendix A**

According to the present theory, $\tau = \frac{1}{K_{\text{MCT}} + K_{\text{hop}}}$ where $K_{\text{hop}} = \frac{1}{a} \exp(-\Delta F/k_B T)$. Even for the simple exponential MCT relaxation the relationship between $K_{\text{MCT}}$ and $\Delta F$ is non trivial [26]. However, in the low temperature limit we can write $K_{\text{MCT}} = \frac{2 \kappa_{\text{hop}}}{\Delta_A^2 + \Delta_B A - 1} = \alpha K_{\text{hop}}$, where $\alpha = \frac{\Delta_A^2 + \Delta_B A - 1}{\Delta_A^2 + \Delta_B A - 1}$. $A$ is the Debye-Waller factor or the form factor (height of the plateau), thus, $\tau = \frac{1}{\alpha + 1} K_{\text{hop}}$. As discussed before, $P_{\text{static}}(\Delta F)$ is Gaussian. The mean barrier height, $\Delta F_\text{s}$, is calculated at $T = T_g$, using Salol parameters. The width of the distribution, $\delta F$, is related to the stretching parameter, $(\beta_{\text{static}}^\text{MCT} = [1 + (\delta F/k_B T)^2]^{-1/2} [26])$ and it is taken in such a way that it gives $\beta_{\text{hop}}^\text{MCT} = 0.5$. With these above mentioned parameters we calculate the total relaxation and fit it to a stretched exponential. From the fitting we obtain $\tau_{\text{KW}}$ and $\beta_{\text{KW}}$. This is now fed into eq[3] to obtain $P_{\text{dynamic}}(\Delta F)$.

**Appendix B**

Since it is found that the mean barrier height is dependent on the configurational entropy and almost independent of the system thus for all the systems [13], we calculate $\Delta F_0$ using Salol parameters ($s_{\text{fit}} = 2.65$, $T_K = 175 K$, $T_o^g = 278 K$). The width of the barrier height distribution is fixed according to the fragility index $D$ which is taken from Bohmer et al. [4]. This then lets us define for each system, the static barrier height distribution and also the stretching in the hopping dynamics. For the Salol system we found that $\tau_o$ has to be used as a fitting parameter to describe the proper timescale of the dynamics. In this calculation we also vary $\tau_o$ for each system in such a way that at $T = T_g$ the relaxation time is of the order of 100s. We find that for more fragile system we need a larger value of $\tau_o$

We now need to define the corresponding MCT dynamics for each system. Above the MCT transition temperature $T_f^{\text{fit}}$, the dynamics is expected to be described completely by the MCT dynamics. Thus the $\beta_{\text{total}}$ above $T_f^{\text{fit}}$ should be equal to the $\beta_{\text{MCT}}$ value. For the systems like Salol [4], Glycerol [29] and Silica [34] where the value of the stretching parameters at high temperatures are known we use those values to find the MCT parameters. For the systems where the stretching parameter at high temperatures are not known we use a reasonable value (definitely larger than $\beta_{\exp}(T = T_g)$ and also vary it in small amount along with $\tau_o$ to get the proper relaxation timescale at $T_g$. As for the value of $T_o^g$ and $T_K$, we keep them same as the Salol system. The $\beta_{\exp}$ values are again obtained from Bohmer et al. for the corresponding $D$ values which are used to describe the hopping dynamics. So our only constrain is that the timescale should be of the order of 100s at $T_g$.

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