Novel Relaxation Patterns in Supercooled Liquids from Generalized Mode-Coupling Theory

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We consider a generalized hierarchical formulation of schematic kinetic equations in which the full basis of multipoint density correlations is taken into account. By varying the parameters that control the effective contributions of higher-order correlations, we show that infinite hierarchies can give rise to both sharp and avoided glass transitions. Moreover, small changes in the form of the coefficients result in different scaling behaviors of the structural relaxation time, providing a means to tune the fragility in glass-forming materials. This demonstrates that the infinite-order construct of generalized mode-coupling theory constitutes a powerful and unifying framework for kinetic theories of the glass transition.

The glass transition of liquids and dense colloidal suspensions represents one of the most puzzling phenomena in all of condensed matter science. Among the various theories of glass formation proposed in the last few decades, mode-coupling theory (MCT) has acquired a unique place in this area of research. In particular, MCT can reproduce important features of the time-dependent dynamics and relaxation of supercooled liquids using only static information as input, making it essentially the only theory of glassy dynamics based entirely on first principles [1, 2].

The main quantity of interest in MCT is the two-point density correlation function \( F(k, t) = N^{-1} \langle \rho_{-k}(0) \rho_k(t) \rangle \), where \( k \) is a wavevector with magnitude \( k \), \( \rho_k(t) \) is the \( k \)-th Fourier component of the spatial density fluctuations at time \( t \), \( N \) is the number of particles, and the brackets denote a canonical ensemble average. The equation of motion for \( F(k, t) \) contains a memory function that, within the standard MCT framework, is assumed to be dominated by pair-densities. This allows one to factorize the memory kernel, which is essentially a four-point density correlator, into a product of two two-point correlators. Applying additional Gaussian and convolution approximations for the static multi-point correlation functions subsequently yields a closed, self-consistent expression for the time evolution of \( F(k, t) \).

One of the successes of standard MCT is its ability to capture the “cage effect” responsible for an intermediate-time plateau in correlation functions and the dramatic slow-down of dynamics upon decreasing the temperature or increasing the density. The scaling properties of \( F(k, t) \) associated with this \( \beta \)-relaxation process are also accurately reproduced. The power-law divergence of the \( \alpha \)-relaxation time (\( \tau \)) predicted by MCT is consistent with experiments and computer simulations, but only in the mildly supercooled regime. A major drawback of the theory is that it predicts an ideal glass transition at relatively high temperatures or low densities. Furthermore, standard MCT cannot account for exponential (Arrhenius) or super-Arrhenius dependences of \( \tau \) in the deeply supercooled regime, and thus cannot describe distinct “strong” and “fragile” glass-forming behaviors, respectively [3].

In an effort to account for activated processes that round off the ideal MCT transition, Das and Mazenko [4] and Götte and Sjögren [5] extended standard MCT by considering additional perturbative couplings to current modes. Although this approach can improve the predicted behavior of standard MCT in the case of strongly supercooled liquids, it does not apply to (hard-sphere) systems undergoing Brownian motion, such as colloidal suspensions, where current modes play no substantial role. Indeed, several recent theoretical and computational studies have disputed the importance of density-current mode coupling close to the glass transition on general grounds [6–8].

An alternative improvement to standard MCT, referred to as generalized MCT (GMCT), was first introduced by Szamel in 2003 [9]. GMCT relies on the fact that the exact time evolution of four-point density correlations is governed by six-point correlation functions, which in turn are controlled by eight-point correlations, and so on. This makes it possible to delay the factorization approximation for the memory kernel to a later stage. Numerical studies employing second- and third-order truncations have shown that GMCT indeed systematically improves the predicted MCT transition temperature (or volume fraction), implying that higher-order correlations account for at least some features ignored by standard MCT in the deeply supercooled regime [9, 10].

More recently, two of us extended the GMCT approach to infinite order using a simplified schematic model based on the form of the microscopic equations of motion, allowing the factorization closure to be rigorously avoided [11]. The general form of this infinite hierarchy reads (see also Ref. [12])

\[
\dot{\phi}_n(t) + \mu_n \phi_n(t) + \lambda_n \int_0^t \phi_{n+1}(\tau) \dot{\phi}_n(t - \tau) d\tau = 0, \quad (1)
\]

where the functions \( \phi_n(t) \) represent normalized \( 2n \)-point density correlators (\( n \in \mathbb{N} \)), \( \mu_n \) are generalized bare frequencies, and the \( \lambda_n \) constants play the role of generalized inverse-temperature-like coupling parameters. In arriving at the form of Eq. (1), we have employed Gaussian and convolution approximations for the static correlations, included only diagonal contributions to the memory functions, and treated all...
wavevectors on an equal footing. In Ref. [11] we considered a simple hierarchy with $\mu_n = n$ and $\lambda_n = \Lambda$, a constant, and found that it admits an analytic solution which is characterized by a continuously growing, exponentially diverging relaxation time. This result is to be contrasted with finite-order GMCT, which always predicts a power-law divergence at a sharp MCT transition. The inclusion of all multipoint dynamical correlations thus provides a means to strictly remove the sharp MCT transition and convert power-law divergences of $\tau$ into exponentially varying forms.

In this Letter, we further elaborate on the infinite schematic GMCT framework and show that, by considering more general forms for the $\mu_n$ and $\lambda_n = \lambda_n(\Lambda)$ parameters of the hierarchy, infinite-order GMCT can also account for standard-MCT-like behavior. More explicitly, we demonstrate that infinite GMCT hierarchies cannot only reproduce the many features of the schematic $F_2$ model—which is characterized by a sharp MCT transition and power-law relaxation [13]—but can also reveal novel relaxation patterns beyond that predicted by standard MCT, even in the case where a finite-coupling glass transition is found. We also discuss how both strong and fragile relaxation motifs can emerge within infinite GMCT hierarchies devoid of sharp transitions by tuning the $n$-dependence of the $\lambda_n$-parameters. This constitutes the first kinetic-theory-motivated framework that can account for different fragilities in glass-forming materials.

Let us first consider some general features of Eq. (1) and its solutions $\{\phi_n(t)\}$. An important quantity in our present discussion is the $\alpha$-relaxation time for the $n$-th level density correlator, which we define as

$$\tau_n = \int_0^\infty \phi_n(t) dt = \hat{\phi}_n(s = 0).$$  

Here $\hat{\phi}_n(s)$ is the Laplace transform of $\phi_n(t)$, defined by

$$\hat{\phi}_n(s) = \mathcal{L}\{\phi_n(t)\} = \int_0^\infty \phi_n(t) e^{-st} dt.$$  

From the Laplace transform of Eq. (1), we find

$$\hat{\phi}_n(s) = \left( s + \frac{\mu_n}{1 + \lambda_n \hat{\phi}_{n+1}(s)} \right)^{-1},$$  

which may be iterated $k$ times for $s = 0$ to yield

$$\tau_n = \frac{1}{\mu_n} \sum_{m=0}^k \prod_{i=0}^{m-1} \frac{\lambda_{n+i}}{\mu_{n+1+i}} + \left( \prod_{i=0}^{k-1} \frac{\lambda_{n+i}}{\mu_{n+i}} \right) \tau_{n+k+1}. \quad (4)$$

This is our general expression for the relaxation time of $\phi_n(t)$ governed by the infinite hierarchy of Eq. (1). Eq. (4) may be simplified by a suitable choice of $\mu_n$ and $\lambda_n$ such that the second term will vanish for $k \to \infty$.

Instead of considering the $\alpha$-relaxation time, one may also characterize the glass transition in terms of the long-time limit of $\phi_n(t)$. We define this long-time limit as $q_n = \lim_{t \to \infty} \phi_n(t) = \lim_{s \to 0} s \hat{\phi}_n(s)$. From Eq. (3) we obtain

$$\frac{1}{q_n} = 1 + \frac{\mu_n}{\lambda_n} \frac{1}{q_{n+1}}, \quad (5)$$

which by iteration becomes

$$\frac{1}{q_n} = \sum_{m=0}^{k-1} \prod_{i=0}^{m-1} \frac{\mu_{n+i}}{\lambda_{n+1+i}} + \left( \prod_{i=0}^{k-1} \frac{\mu_{n+i}}{\lambda_{n+i}} \right) \frac{1}{q_{n+k+1}}. \quad (6)$$

Analogous to Eq. (4) in the limit of $k \to \infty$, the second term vanishes if $\mu_n$ and $\lambda_n$ are chosen appropriately.

The convergence behavior of the general expressions (4) and (6) can already reveal important information on the type of transition contained in the hierarchy. For an MCT-like transition, there exists a critical point $\Lambda = \Lambda_c$ above which the $\phi_n(t)$ no longer decay to zero. This nonzero long-time limit $q_n$ may grow continuously (type-A transition) or discontinuously (type-B transition) as a function of $\Lambda$. If the transition is completely avoided, the relaxation time grows continuously but ultimately leads to full relaxation of the correlation functions ($q_n = 0$) for all finite $\Lambda$. One may verify that [neglecting the second term in Eqs. (4) and (6)] the series for $\tau_n$ converges if $\lim_{n \to \infty} \lambda_n/\mu_{n+1} < 1$, and $1/q_n$ converges if $\lim_{n \to \infty} \mu_n/\lambda_n < 1$. A type-A transition is characterized by a diverging series for both $\tau_n$ and $1/q_n$ at $\Lambda = \Lambda_c$, while a type-B transition has a diverging $\tau_n$ series and converging $1/q_n$ series. Conversely, for a rigorously avoided transition, $\tau_n$ converges and $1/q_n$ diverges for all $\Lambda$. Thus, depending on the asymptotic behavior of the $\{\mu_n, \lambda_n\}$ coefficients, the GMCT framework can account for all of these physically distinct phenomena. This is one of the key results of this Letter: by making a suitable choice for $\mu_n$ and $\lambda_n$, we can generate arbitrary types of transitions and, by virtue of Eqs. (4) and (6), arbitrary scaling behaviors of the relaxation time and long-time limit. The chosen set of $\{\mu_n, \lambda_n\}$ coefficients subsequently determines the full hierarchy and all its time-dependent solutions $\{\phi_n(t)\}$.

In the remainder of this paper, we shall focus on some explicit examples of the general hierarchy (1) and restrict our discussion to the two-point density correlator $\phi_1(t)$, i.e. $n = 1$. All other correlation functions ($n > 1$) appear only as generalized memory functions for $\phi_1(t)$. We first consider a class of hierarchies that exhibit MCT-like, type-B transitions but are fundamentally distinct from the standard-MCT $F_2$ model. Note that the $F_2$ model is essentially the lowest-order truncation of GMCT with closure $\phi_2(t) = \phi_1^2(t)$ and $\lambda_1 = 4\mu_1\Lambda$. We start with a relatively simple infinite hierarchy of the form $\mu_n = n$ and $\lambda_n = \Lambda(n+c)$, where $c > 0$. The choice $\mu_n = n$ follows naturally from the microscopic derivation of Eq. (1), provided that no explicit distinction is made between different wavevectors (see Refs. [3,12]). In the limit $k \to \infty$, we obtain for the relaxation time $\tau_1$ [see Eq. (4)]

$$\tau_1 = \sum_{m=0}^{\infty} \frac{\prod_{i=1}^{m} (i + c)}{(1 - \Lambda)^{i+1}} \lambda_m,$$

which diverges, to leading order, as $\tau_1 \sim (1 - \Lambda)^{-c}$ near the
critical point $\Lambda_c = 1$. Thus, our infinite hierarchy with parameters $\{\mu_n = n, \lambda_n = \Lambda(n+c)\}$ predicts a power-law divergence of the $\alpha$-relaxation time, similar to the type-B transition in standard MCT. In fact, setting $c$ equal to the standard-MCT $\alpha$-exponent $\gamma \approx 1.765$ yields exactly the same power-law behavior, implying that certain features of the schematic $F_2$ MCT model can be accurately reproduced by a very simple infinite GMCT hierarchy.

Let us now consider the long-time limit of the density-density correlation function $\phi_1(t)$ within this class of hierarchies. From Eq. (6), and taking the limit $k \to \infty$, we find

$$\frac{1}{q_1} = \sum_{m=0}^{\infty} \left( \prod_{i=1}^{m} \frac{i}{i+c} \right) \left( \frac{1}{\Lambda} \right)^m. \quad (8)$$

Explicitly, for a hierarchy with $c = 0$, the inverse plateau height scales with $\Lambda$ as $1/q_n = \Lambda/(\Lambda - 1)$ for all $n$, the case $c = 1$ gives rise to logarithmic scaling, $1/q_1 = \Lambda \log[\Lambda/(\Lambda - 1)]$, and for $c = \gamma$ we have (see Supplemental Material)

$$\frac{1}{q_1} = \frac{\gamma}{\gamma - 1} \left( 1 + \frac{\pi(\gamma - 1)}{\sin(\pi\gamma)} (\Lambda - 1)^{\gamma - 1} + O(\Lambda - 1) \right). \quad (9)$$

In all cases, $q_1 > 0$ for $\Lambda > 1$, confirming that these GMCT hierarchies induce something akin to type-B transitions at the critical point $\Lambda_c = 1$ [1]. The expressions for $q_1$ should, however, be contrasted with the $F_2$ model, which predicts a square-root scaling of the form $q_1^{F_2} = (1 + \sqrt{1 - 1/\Lambda})/2$. Thus, standard-MCT-like hierarchies with $\{\mu_n = n, \lambda_n = \Lambda(n+c)\}$ reveal entirely novel scaling behavior of the plateau height near the transition.

One may also ask whether it is possible to find an infinite hierarchy that exhibits precisely the same $\Lambda$-dependence as the $F_2$ model, both with respect to $q_1$ and $\tau_1$. A comparison between the Taylor series of $1/q_1^{F_2}$ and Eq. (5) reveals that such an exact mapping requires (see Supplemental Material)

$$\lambda_n/\mu_n = \frac{2n + 2}{2n - 1} \Lambda. \quad (10)$$

This type of hierarchy corresponds to a relaxation time

$$\tau_1 = \frac{1}{\mu_1} + \sum_{m=1}^{\infty} \frac{1}{\mu_{m+1}} \left( \prod_{i=1}^{m} \frac{2i + 2}{2i - 1} \right) \Lambda^m. \quad (11)$$

We may now relax the $\mu_n = n$ constraint and fit Eq. (11) to the power-law relaxation time of the $F_2$ model, $\tau_1^{F_2} = \Lambda(1 - \Lambda)^{-\gamma}$, with $\Lambda \approx 1.2573$ a numerical constant (we set $\mu_1 = 1$ in the $F_2$ model). Taking the ansatz $\tau_1(\Lambda) = 1 + \sum_{m=1}^{\infty} \Lambda^m \prod_{i=1}^{m} (i + a)/(i + b)$ yields for the $\mu_n$ parameters (see Supplemental Material)

$$\mu_n = \prod_{i=1}^{n-1} \frac{(2i + 2)(i + b)}{(2i - 1)(i + a)}, \quad (12)$$

with $a \approx 0.52726$ and $b \approx -0.23772$ determined numerically from the fit. Thus, an infinite GMCT hierarchy with coefficients (10) and (12) represents a numerically motivated approximation to the $F_2$ model.

Figure 1 compares the functions $\phi_1(t)$ obtained from the various MCT-like hierarchies discussed above, and from the exact $F_2$ model [13], for different values of $\Lambda$. The GMCT hierarchies were truncated after $N = 10000$ levels by exponential closure [$\phi_N(t) = \exp(-N\tau_1)$], which is ample sufficient to ensure convergence of the numerical solutions. All data were obtained using the time-integration algorithm of Fuchs et al. [14]. For all values of $\Lambda$ considered, the hierarchy with $\{\mu_n = n, \lambda_n = \Lambda(n+\gamma)\}$ exhibits clear deviations from the $F_2$ model, while the numerically fitted GMCT hierarchy [Eqs. (10) and (12)] show remarkable agreement with the exact $F_2$ result. In fact, the fitted hierarchy nearly reproduces the complete time dependence of $\phi_1(t)$ over all 6 decades of time. This is a remarkable and highly non-trivial result: by fitting only the $\{\lambda_n, \mu_n\}$ parameters to a certain plateau height and relaxation time, we capture all qualitative and quantitative features of a finite-order schematic MCT model, both as a function of time and of $\Lambda$.

![FIG. 1: Density-density correlation functions $\phi_1(t)$ for the $F_2$ model (solid lines), the fitted GMCT hierarchy with coefficients (10) and (12) (circles), and the GMCT hierarchy with $\{\mu_n = n, \lambda_n = \Lambda(n+\gamma)\}$ (dashed lines), calculated for $\Lambda = 0.4, 0.9, 1$ and 1.2.](image)
elsewhere [11], is a special case of this type of hierarchy. For this choice of parameters, the second term in Eqs. (4) and (6) also vanishes for $k \to \infty$, and the relaxation time becomes

$$\tau_1 = \sum_{k=1}^{\infty} \frac{1}{[k!]^\nu} \lambda_k^{k-1}.$$  \hspace{0.5cm} (13)

After some manipulation (see Supplemental Material), we obtain

$$\tau_1(\Lambda) \sim \frac{(2\pi)^{(1-\nu)/2}}{\nu^{1/2}} \Lambda^{2/\nu} \exp(\nu \Lambda^{1/\nu}),$$  \hspace{0.5cm} (14)

where we have assumed that $\Lambda \gg 1$. This assumption holds in the deeply supercooled regime, i.e. at asymptotically low temperatures. It is important to remark that, in contrast to the standard MCT prediction, the relaxation time of Eq. (14) does not diverge at any finite $\Lambda$. This implies that there is no sharp MCT transition at any finite $\Lambda$ for an infinite GMCT hierarchy of the form $\lambda_n = \Lambda n^{1-\nu}$. Instead the relaxation time grows continuously with $\Lambda$, as was already found in Ref. [11] for the special case $\nu = 1$. It may be verified that the long-time limit of $\phi_1(t)$ for this class of hierarchies also vanishes for all $\Lambda, \nu > 0$, confirming that the transition is rigorously avoided.

In the deeply supercooled regime, the true relaxation time diverges as an Arrhenius or super-Arrhenius law, depending on the fragility of the system. It is well established that standard MCT cannot account for such fragilities, and instead always predicts a power-law divergence of $\tau_1$. Inspection of Eq. (14) reveals, however, that the relaxation time increases more dramatically as a function of $\Lambda$ when $\nu$ approaches 0. This is the analog of the system becoming more fragile as $\nu$ is decreased. This is an important result: the $n$-dependence of the coupling strengths $\lambda_n$ in infinite-order GMCT provides a means to tune the fragility of a glass-forming system. While this finding is based on only a schematic description of the dynamics, we expect it to be preserved in a fully microscopic version of GMCT, similar to how the qualitative features of the schematic $F_2$ model are reproduced in $k$-dependent standard MCT.

Finally, let us look at some explicit examples of the GMCT solutions with $\mu_n = n$ and $\lambda_n = \Lambda n^{1-\nu}$ ($\Lambda, \nu > 0$). For $\nu = 1$ ($\lambda_n = \Lambda$), we recover the hierarchy of Ref. [11], with $\tau_1(\Lambda) \sim \exp(\Lambda)/\Lambda$. The case $\nu = 2$ ($\lambda_n = \Lambda/n$) yields, from Eq. (13) (see Supplemental Material), $\tau_1 = I_1(2\sqrt{\Lambda})/\sqrt{\Lambda}$, where $I_1$ is the modified Bessel function of the first kind. For large $\Lambda$, the relaxation time then behaves as $\tau_1 \sim (4\pi)^{-1/2} \Lambda^{3/4} \exp(2\sqrt{\Lambda})$, in accordance with Eq. (14).

The density correlation functions $\phi_1(t)$ for these two hierarchies, as well as those for $\nu = 1/2$, are shown in Fig. 2 for various values of $\Lambda$. The data have been obtained from numerical integration of the hierarchical equations using the algorithm of Ref. [14] with exponential closure at $N = 1000$. One can see that, for fixed $\Lambda$, the correlation functions decay more rapidly as $\nu$ increases, as predicted by Eq. (14). The difference in fragility between hierarchies with different $\nu$ is best observed by examining the relaxation times $\tau_1$ as a function of $\Lambda$ [Fig. 2(d)]. These data were generated by numerically integrating the $\phi_1(t)$ over time [Eq. (2)]. It is clear that hierarchies with small $\nu$ give the most fragile behavior, i.e. the relaxation time increases more dramatically with varying $\Lambda$ as $\nu$ approaches zero. For comparison, we also show the analytical expression for $\tau_1$ [Eq. (14)] in Fig. 2(d); the agreement with the numerical data is seen to be very good for $\Lambda > 1$. As a final point, we note that other features of $\phi_1(t)$ are also affected by $\nu$, e.g. the plateau height of $\phi_1(t)$ in the $\beta$-relaxation regime. In fact it has been noted that strong glass formers generally have larger plateau values compared to fragile ones [15]. The precise characterization of these features will be discussed in future work.

In summary, we have presented a schematic generalized mode-coupling theory in which multipoint density correlations are included through an infinite hierarchy of coupled equations [6,11]. Such a hierarchical framework can accurately capture the features of the standard-MCT $F_2$ model, but can also give rise to generalized new forms of MCT-like transitions, suggesting that infinite-order GMCT is a general framework unifying and extending mode-coupling-like theories of glassy behavior. Moreover, a suitable choice of the coupling strengths of the higher-order correlations can lead to Arrhenius and super-Arrhenius behavior of the $\alpha$-relaxation time, providing a means to tune the degree of fragility with a single parameter. This represents the first MCT-based theory that can account for different fragilities in glass-forming materials. In future research, we seek to connect the level-dependent coupling strengths to specific materials, thus exploring the microscopic origin of the different types of GMCT.

FIG. 2: Solutions $\phi_1(t)$ of infinite hierarchies with $\mu_n = n$ and $\lambda_n = \Lambda n^{1-\nu}$ for (a) $\nu = 2$ and $\Lambda = 0, 1, \ldots, 10$, (b) $\nu = 1$ and $\Lambda = 0, 1, \ldots, 10$, (c) $\nu = 1/2$ and $\Lambda = 0, 1, \ldots, 5$. The fastest decaying functions correspond to $\Lambda = 0$. Panel (d) shows the associated relaxation times $\tau_1(\Lambda)$. The solid lines were obtained by numerical integration of $\phi_1(t)$ over time [Eq. (2)], and the circles represent the analytical result of Eq. (14).
hierarchies.

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