Tagged-particle motion of Percus-Yevick hard spheres from first principles

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Tagged-particle motion of Percus–Yevick hard spheres from first principles

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ABSTRACT
We develop a first-principles-based generalized mode-coupling theory (GMCT) for the tagged-particle motion of glassy systems. This theory establishes a hierarchy of coupled integro-differential equations for self-multi-point density correlation functions, which can formally be extended up to infinite order. We use our GMCT framework to calculate the self-nonergodicity parameters and the self-intermediate scattering function for the Percus–Yevick hard-sphere system based on the first few levels of the GMCT hierarchy. We also test the scaling laws in the \( \alpha \)- and \( \beta \)-relaxation regimes near the glass-transition singularity. Furthermore, we study the mean-square displacement and the Stokes–Einstein relation in the supercooled regime. We find that qualitatively our GMCT results share many similarities with the well-established predictions from standard mode-coupling theory, but the quantitative results change, and typically improve, by increasing the GMCT closure level. However, we also demonstrate on general theoretical grounds that the current GMCT framework is unable to account for violation of the Stokes–Einstein relation, underlining the need for further improvements in the first-principles description of glassy dynamics.

I. INTRODUCTION

Glassy dynamics are displayed in many systems on different length scales, such as atoms, colloids, granules, and even living cells. Since the 1980s, an increasing number of theories and models have been proposed to explain the emergence of glassy dynamics, but the nature of the glass transition is still fiercely debated today. One of the main challenges is to relate the tremendous slowdown of the dynamics of glass-forming materials to the only minor microstructural changes observed during supercooling or compression. The mode-coupling theory (MCT) of the glass transition is one of the few first-principles-based theories to describe glassy dynamics using only static structures as input. This theory successfully qualitatively and semi-quantitatively predicts the intermediate scattering functions (ISFs) and the self-intermediate scattering functions (SISFs) from the static structure factors for many glass-forming materials and as such is able to reproduce the celebrated scaling laws characterizing the two-step decay of the ISF and SISF near the glass transition point.

However, MCT invokes an uncontrolled factorization approximation that dismembers potentially important information covered in higher-order density correlations. Recently, a new theory called generalized mode-coupling theory (GMCT) has therefore been developed to remove or at least reduce the influence of this uncontrolled approximation. The basic idea is to develop exact equations of motion for the higher-order dynamic density correlations (instead of factorizing them) so that a hierarchy of equations similar to MCT is developed. Early results have demonstrated that the predicted ISFs are systematically improved as more higher-order density correlators are included within the framework of GMCT. Moreover, the scaling laws predicted in MCT, which qualitatively agree with simulations and experiments, are preserved in GMCT with quantitatively improved exponent parameters.

Up until now, studies involving GMCT have only focused on the ISF, i.e., the dynamics of collective motion. The motion of a single tagged particle is, however, equally important and can reveal complementary information about the dynamics. From a practical point of view, the SISF can also offer better statistical quality. Indeed, since all particles are, in principle, statistically equivalent to the tagged one, it is generally much easier to reliably obtain the SISF from experiments or simulations than the ISF. This advantage of the
SISF has rendered it a widely used quantity for comparison and testing of experiments and simulations with MCT during the past few decades.\textsuperscript{[22–24]}

From both experiments and simulations, it is known that the scaling laws of the SISF are similar to those of the ISF.\textsuperscript{[12]} In particular, there are two time scales for the two-step decay of the SISF: (i) a time scale \(\tau_\beta\) characterizing the \(\beta\)-relaxation regime and (ii) a time scale \(\tau_\alpha\) characterizing the \(\alpha\)-relaxation regime. Both \(\tau_\beta\) and \(\tau_\alpha\) follow a power law with respect to the reduced packing fraction (or reduced temperature) and the exponents of these two power laws are related to each other. The dynamics of the SISF satisfy factorization scaling laws regarding wavenumbers and time in the \(\beta\)-relaxation regime and the time–density (or time–temperature) superposition principle in the \(\alpha\)-relaxation regime.\textsuperscript{[22,23,25]} The dynamics of the \(\alpha\)-relaxation regime can also be well described by the stretched-exponential Kohlrausch function.\textsuperscript{[12]} All these scaling laws are successfully reproduced within MCT, but the exponent parameters are generally not accurate.\textsuperscript{[23,25,26]}

To systematically improve upon these results, a GMCT framework for the tagged-particle motion and the SISF is, therefore, required.

An important byproduct from the study of the SISF is that we can naturally extract and check the Stokes–Einstein relation (SER). The original SER relates the single-particle diffusion coefficient \(D\), the shear viscosity \(\eta\), and the temperature \(T\) to each other via \(D\eta/T = \text{constant}\). Typically (although not always correctly), it is assumed that \(\tau \propto \eta\) or \(\tau \propto \eta^2/T\), which follows if the instantaneous shear modulus is temperature-independent or if a Gaussian solution to the diffusion equation is used, respectively.\textsuperscript{[27]} In the present work, we will assume these relations to hold and interpret \(D\tau = \text{constant}\) as an effective SER. From simulations and experiments, however, it is known that the SER becomes significantly violated during vitrification.\textsuperscript{[22–24,27–30]} This violation is generally regarded as a manifestation of dynamical heterogeneity although some controversy still exists on its physical origins.\textsuperscript{[41]} Unfortunately, in MCT, where \(\tau\) is obtained from the SISF and \(D\) from the mean-squared displacement (MSD) (which is directly related to the SER for vanishing wavenumber \(k \rightarrow 0\)), the violation of the SER does not appear or only shows up very weakly.\textsuperscript{[23,25,28,29]} Based on the qualitatively similar asymptotic scaling laws within collective GMCT compared to MCT,\textsuperscript{[18]} we expect that, in the framework of GMCT for tagged-particle motion, the SER will also be preserved close to the critical point. It could, however, be broken upon departing from the critical point, similar to what is observed in MCT.

The goal of this work is to develop and test GMCT for the tagged-particle motion. We take a monodisperse system of dense hard spheres as our reference system, with the static structure factors tagged-particle motion. We take a monodisperse system of dense hard spheres as our reference system, with the static structure factors

II. THEORY

A. GMCT of collective motion

We start by summarizing the microscopic GMCT equations of collective motion.\textsuperscript{[16]} Briefly, the theory seeks to describe spatiotemporal correlations in the density field (as encoded in the ISF) through the repeated and hierarchical application of the Zwanzig–Mori projection operator formalism;\textsuperscript{[14,35]} each successive projector is built from an increasingly large basis of multi-point density modes. The dynamical objects of interest are thus the \(2n\)-point density correlation functions \(F_n(\{k\}_{1:2n},t\), which are given by

\[
F_n(\{k\}_{1:2n},t) = \langle \rho_{-k_1}(0)\ldots\rho_{-k_n}(0)\rho_{k_1}(t)\ldots\rho_{k_n}(t) \rangle.
\]

Here, \(\{k\}_{1:2n}\) denotes a set of \(n\) wavevectors \(k_1, k_2, \ldots, k_n\), \(\rho_k(t) = \sum_{\ell=1}^{N_p} e^{i k \cdot r_\ell(t)}/\sqrt{N_p}\) represents a collective density mode with wavevector \(k\) at time \(t\); \(r_\ell\) is the position of particle \(j\); and \(N_p\) is the total number of particles. The angular brackets denote an ensemble average, and the label \(n (n = 1, \ldots, \infty)\) specifies the level of the GMCT hierarchy. For convenience, we will neglect the subscript \(1 \leq i \leq n\) in the following. Note that for \(n = 1\), \(F_1(k,t)\) is the usual intermediate scattering function.

In the overdamped limit, the GMCT equations read

\[
v_a F_n(\{k\}_{1:2n},t) + F_n(\{k\}_{1:2n},t)S_n^{-1}(\{k\}_{1:2n})\mu_n(\{k\}_{1:2n}) + \int_0^t F_n(\{k\}_{1:2n},t-u)S_n^{-1}(\{k\}_{1:2n})M_n(\{k\}_{1:2n},u)du = 0,
\]

where \(v_a\) is an effective friction coefficient,

\[
S_n(\{k\}_{1:2n}) = F_n(\{k\}_{1:2n},t = 0) = \prod_{j=1}^n S(k_j)\]

are \(2n\)-point static density correlation functions that serve as the \(t = 0\) boundary conditions and that are usually approximated in terms of the static structure factors \(S(k_j)\), and

\[
J_n(\{k\}_{1:2n}) = \int \frac{D_0k^2}{S(k)} \prod_{j=1}^n S(k_j)
\]

with \(D_0\) denoting the bare diffusion coefficient. The memory functions are given by

\[
M_n(\{k\}_{1:2n},t) = \frac{\rho D_0}{2} \int \frac{dq}{(2\pi)^2} \sum_{j=1}^n \left| V_{qk-qj} \right|^2 
\]

\[\times F_{n+1}(\{k_j - q_j\}, \{k_{i=1}^{n-1}\}, t),\]

where \(\rho\) is the number density, \(\{k_{i=1}^{n-1}\}\) represents the set of \(n - 1\) wavenumbers in \(\{k_1, \ldots, k_n\}\) except \(k_j\), and \(V_{qk-qj}\) are the static
vertices that represent wavevector-dependent coupling strengths. The vertices are defined as

$$V_{q,k} = (q \cdot k) \phi(q) + k \cdot (k - q) \phi(k - q),$$  \hspace{1cm} (6)

with $\phi(q)$ denoting the direct correlation function, which is related to the static structure factor via $\phi(q) = [1 - 1/S(q)]/\rho$. Note that within GMCT, the ISF is thus governed by $F_s(k, t)$, which in turn is controlled by $F_s(k, t)$, etc. For additional details on, e.g., the GMCT derivation, closure approximations, and numerical solutions for $F_n(k, t)$, we refer to Refs. 16–18.

B. GMCT of a tagged particle

The dynamics of a tagged particle can be quantified by its SISF, $F_0(k, t) = \langle \rho_{s,0}(0) \rho_{s,0}^*(t) \rangle$, where $\rho_{s,0}(t) = e^{\omega_s(t)}$ is the tagged-particle density mode at wavevector $k_0$ and $r$ denotes the particle position. Note that we label the SISF with the subscript 0; generally, we use the subscript $n$ to indicate the number of collective density modes in the correlator. The exact equation of motion for $F_0(k, t)$ is derived in MCT and given by

$$\nu_0 F_0(k, t) + F_0(k, t) \{ S_0(k, t) \}^{-1} F_0(k_0)$$

$$+ \int_0^t F_0(k, t - u) \{ F_0(k_0) \}^{-1} M_0(k, u) du = 0. \hspace{1cm} (7)$$

Here, $\nu_0$ is an effective friction coefficient for the tagged particle, $S_0(k, t) = 1$, and $F_0(k_0) = D k_0^2$ with $D$ being the short-time diffusion coefficient of the tagged particle. Note that $D_0 = D$; if we take the tagged particle to be one of the particles in the system. The memory function yields

$$M_0(k_0, t) = \rho(D_0)^2 \int \frac{d\mathbf{q}}{(2\pi)^3} |V_{q,k_0}^*|^2 F_1(|k_0 - \mathbf{q}|, q, t)$$

and is written in terms of the vertex

$$V_{q,k_0}^* = q \cdot k_0 \phi(q)$$

and the tagged-particle four-point density correlation function

$$F_1(k_0, k_1, t) = \langle \rho_{s,0}(0) \rho_{s,0}(0) \rho_{s,0}^*(t) \rho_{s,0}(t) \rangle. \hspace{1cm} (10)$$

Note that this density correlator contains both tagged-particle and collective density modes; physically, this is due to the fact that the motion of a single particle is also inherently governed by the collective dynamics of its environment.

In standard MCT, one uses the factorization approximation

$$F_1(k_0, k_1, t) = F_0(k_0, t) \times F_1(k_1, t)$$

such that Eq. (7) for $F_0(k_0, t)$ can be solved self-consistently together with the MCT equation for $F_1(k_1, t)$. However, the factorization approximation is uncontrolled, and here we avoid it by instead developing an exact equation of motion for $F_1(k_0, k_1, t)$. Generalizing this concept, we can define the $n$-th order tagged-particle multi-point density correlation functions, which read

$$F_n(k_0, k_1, \ldots, k_n, t) = \langle \rho_{s,0}(0) \rho_{s,0}(0) \ldots \rho_{s,0}(0) \rangle$$

$$\times \rho_{s,0}(t) \rho_{s,0}(t) \ldots \rho_{s,0}(t), \hspace{1cm} n \geq 1. \hspace{1cm} (12)$$

Here, our notation convention for $n$ implies that the correlators $F_n(k_0, t)$ and $F_n(k_0, \{ k_i \}, t)$ contain the same number of collective density modes; the difference between $F_n(k_0, t)$ and $F_n(k_0, \{ k_i \}, t)$ is thus $\rho_{s,0} \rho_{s,0}^*(t)$. The exact equations of motion for $F_n(k_0, \{ k_i \}, t)$ can be derived using the Zwanzig–Mori projection operator formalism analogous to the collective case, and they take on a similar form, i.e.,

$$v_s F_n(k_0, \{ k_i \}, t) + F_n(k_0, \{ k_i \}) \{ S_n(k_0, \{ k_i \}) \}^{-1} F_n(k_0, \{ k_i \})$$

$$+ \int_0^t F_n(k_0, \{ k_i \}, t - u) \{ F_n(k_0, \{ k_i \}) \}^{-1} M_n(k_0, \{ k_i \}, u) du = 0, \hspace{1cm} (13)$$

where

$$S_n(k_0, \{ k_i \}) = F_n(k_0, \{ k_i \}, 0) = S_n(\{ k_i \}) \approx \sum_{j=1}^n S(k_j), n \geq 1. \hspace{1cm} (14)$$

and

$$F_n(k_0, \{ k_i \}) = \int \frac{d\mathbf{q}}{(2\pi)^3} |V_{q,k_0}^*|^2 F_{n+1}(|\mathbf{k}_0 - \mathbf{q}|, q, \{ k_i \}, t)$$

$$\times \rho(D_0)^2 \int \frac{d\mathbf{q}}{(2\pi)^3} \sum_{j=1}^n |V_{q,k_j}|^2$$

$$\times F_{n+1}(k_j, |\mathbf{k}_j - \mathbf{q}|, q, \{ k_{i,j} \}) \{ F_{n+1}(k_j, |\mathbf{k}_j - \mathbf{q}|, q, \{ k_{i,j} \}) \}^{-1} du = 0. \hspace{1cm} \{ F_{n+1}(k_j, |\mathbf{k}_j - \mathbf{q}|, q, \{ k_{i,j} \}) \}^{-1} \hspace{1cm} \{ F_{n+1}(k_j, |\mathbf{k}_j - \mathbf{q}|, q, \{ k_{i,j} \}) \}^{-1} \hspace{1cm} (16)$$

Here, $V_{q,k_0}^*$ is the same vertex as in the collective case [Eq. 10] and $V_{q,k_j}^*$ is the self vertex [Eq. 9] in the memory function of MCT for the tagged particle.

In principle, the hierarchy of GMCT equations can continue up to infinite order, but in practice, due to limited computing power, we have to choose a closure at a finite level $N$, similar to what has been done in GMCT for the collective particle motion. Following earlier work, we may consider two types of closure approximations. One type is the exponential closure, which simply cuts off the hierarchy by setting $F_n(k_0, \{ k_i \}, t) = 0$, such that $F_{N+1} \sim \exp(t/\tau_{N+1})$ with $\tau_{N+1} = \nu_0 / \rho(D_0)^2$. As a consequence, $F_n(t)$ will always decay to zero, and this GMCT closure approximation typically leads to an underestimation of the true dynamics, i.e., yielding too fast relaxation.

The other type of closure is a so-called mean-field (MF) closure, approximating $F_n(k_0, \{ k_i \}, t)$ by a combination of density correlation functions at lower levels. An example of such a MF closure is

$$F_N(k_0, \{ k_i \}, t) = F_0(k_0, t) F_N(\{ k_i \}, t). \hspace{1cm} (17)$$

In contrast to the exponential closure, an MF closure can produce a sharp glass transition but it tends to overestimate the dynamics, thus generally predicting too slow relaxation. When $N \to \infty$, we expect the GMCT predictions under the two types of closures to
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localization length \( r \)

Invoking Eq. (18), we obtain the following expression for which corresponds to the following asymptotic value of the MSD:

\[
\lim_{t \to \infty} \delta r^2(t) = 6D_0 t,
\]

where

\[
M_{\text{MSD}}(t) = \lim_{k_0 \to 0} \frac{M_0(k_0, t)}{(D_0)^2 k_0^2} = \lim_{k_0 \to 0} \rho \int_{k_0}^{\infty} \frac{d^3 q}{(2\pi)^3} \frac{|V_{\rho} k_0|^2}{k_0^2} F_s(|q|, q, t).
\]

Carrying out the limit \( k_0 \to 0 \), we finally obtain the memory functions for the MSD,

\[
M_{\text{MSD}}(t) = \frac{\rho}{6\pi} \int_0^\infty p^2 \tilde{c}(p) F_s(p, p, t) dp.
\]

Using Eqs. (18) and (20) with the calculated \( F_s(p, p, t) \) from GMCT for the tagged-particle motion as an input, the MSD can be calculated numerically.

There is a diffusion–localization transition for the MSD, which can be characterized by its long-time limit. In the liquid state, the particle always migrates diffusively in the long-time limit with a constant MSD, which physically indicates relatively slow dynamics.

\[
D' = D_0 \left[ 1 + \frac{D_0}{\rho} \int_0^\infty \frac{M_{\text{MSD}}(u)}{u} du \right]^{-1}.
\]

However, in the glass state, the tagged particle is localized, which is manifested by a constant MSD at long times. A characteristic localization length \( r_c \) can then be defined via

\[
F_0(k_0) = 1 - (k_0 r_c)^2 + O(k_0^4),
\]

which corresponds to the following asymptotic value of the MSD:

\[
\lim_{t \to \infty} \delta r^2(t) = 6r_c^2.
\]

Invoking Eq. (18), we obtain the following expression for \( r_c \):

\[
r_c^2 = 1/M_{\text{MSD}}(t \to \infty).
\]

D. Numerical details

Overall, Eqs. (2), (7), (13), and (18) allow us to obtain the ISF, SISF, and MSD for a glass-forming material using the corresponding static structure factors \( S(k) \) as the only input. Here, we study these GMCT equations for a monodisperse Percus–Yevick hard-sphere system using the packing fraction \( \varphi \) as our control parameter. We numerically solve the dynamical equations on an equidistant wavenumber grid of 100 points ranging from \( kd = 0.2 \) to \( kd = 39.8 \), where \( d \) is the diameter of the particle. The integrals over the wavevector \( q \) in the memory functions Eqs. (5) and (16) and \( p \) in Eq. (20) are approximated as a double and single Riemann sum, respectively. For the time-dependent integration, we apply the fast algorithm\(^{25,27} \) with a starting time step size \( \Delta t = 10^{-6} \) that is doubled every 32 points. We assume \( D_0 = D_0' = 1 \) and set \( \nu_0 = \nu_0' = 1 \) for all \( n \).

III. RESULTS AND DISCUSSION

A. Self-non-ergodicity parameters

We first consider the long-time limit of the SISF, i.e., the self-non-ergodic parameter, at the glass transition point. We define the critical point \( \varphi_c \) as the lowest packing fraction where the long-time limit of the SIF is larger than zero. From previous GMCT studies for the collective dynamics of hard spheres,\(^{13,15,17} \) it is known that the critical glass transition point increases with the GMCT closure level \( N \) in a seemingly convergent manner. Here, we find identical values for \( \varphi_c \) as predicted from the SISF, see Table I. We note, however, that in general, the location of the glass transition point can be different for the ISF and SIF, as is the case for binary hard-sphere mixtures.\(^{40} \) In Fig. 1, we plot the self-non-ergodic parameter \( f_{\varphi}^s(k) \) (solid lines) at the respective GMCT critical points for \( N = 2, 3, \) and 4. For comparison, we also show the corresponding collective non-ergodic parameters \( f_{\varphi}^c(k) \) (dashed lines in Fig. 1). It can be seen that \( f_{\varphi}^c(k) \) increases with increasing \( N \) for nearly all wavenumbers \( k \), which physically indicates relatively slow dynamics of a tagged particle. This trend is also consistent with the behavior seen in the collective density correlators \( f_{\varphi}^s(k) \).\(^{17} \)

In simulations, it is difficult to retrieve \( f_{\varphi}^s(k) \) precisely, and instead, one often uses the plateau values \( A(k) \) obtained from fitting the SISF to the so-called Kohlrausch and von Schweidler functions [see also Eq. (33)]. These plateau values should be roughly equal to \( f_{\varphi}^c(k) \) albeit slightly smaller.\(^{34,41} \) However, previous simulations of weakly polydisperse hard spheres\(^{23} \) have demonstrated that, for wavenumbers \( kd \gt 10 \), the theoretically predicted \( f_{\varphi}^c(k) \) from MCT is, in fact, smaller than the corresponding \( A(k) \). This discrepancy could be fixed using GMCT since the self-non-ergodicity parameters \( f_{\varphi}^s(k) \) predicted from higher-order GMCT are larger than the ones from MCT, and they can also become larger than

\hspace{1cm}

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TABLE I. Predicted critical packing fractions \( \varphi_c \) and parameters \( y, a, b, \) and \( \lambda \) determined from the SISFs for Percus–Yevick hard spheres obtained for different GMCT mean-field closure levels \( N \). The data for \( N = 5 \) are taken from Ref. 17 for the ISF and are assumed to be preserved for the SISF.
the $A(k)$ from simulations. This needs to be tested with a GMCT for multicomponent systems in the future,\textsuperscript{31} but the trend of our $f^sc(k)$ suggests that GMCT could (at least partly) remedy this inconsistency.

In MCT, i.e., when $N = 2$, the $f^sc(k)$ can be well described by a Gaussian $f^sc_0(k) = e^{-k^2d^2}$ up to $kd = 15$ (black dotted lines in Fig. 1).\textsuperscript{32} However, with higher closure level $N$, deviations from the Gaussian approximation start to occur at much smaller wavenumbers and also become larger (blue and red dotted lines in Fig. 1). This might reflect some traits of dynamical heterogeneity, i.e., non-trivial spatiotemporal correlations in the density, which could be embedded in the higher-order density correlators that are explicitly included in GMCT.

Finally, we have also plotted the long-time limit of the density correlators one level above $f^{sc}_0(k)$, i.e., $f^{sc}_N(k, k)$, in Fig. 1 (dashed-dotted lines). At all closure levels $N$, $f^{sc}_1(k, k)$ is modulated by the structure of $S(k)$ with a maximum at $kd \approx 7.4$. This is natural for MCT since $f^{sc}_1(k, k) = f^{sc}_0(k) \times f^2_s(k)$ and $f^2_s(k)$ is strongly modulated by $S(k)$. A salient feature of the $f^{sc}_1(k, k)$ GMCT curves in Fig. 1 is that they do not show a monotonic change with the closure level $N$; rather, we find crossovers at several wavenumbers $k$ where the ordering of the $f^{sc}_1(k, k)$ curves changes. We speculate that this behavior, which is also exhibited by the collective GMCT analogs $f^sc_1(k, k)$,\textsuperscript{33} might hint at the presence of dynamical heterogeneities, but further research is needed to elucidate the microscopic origins of these $N$-dependent crossovers.

B. Time-dependent relaxation dynamics of the SISF

We now seek to study the time-dependent self-intermediate scattering functions $F^0_{sc}(k_0, t)$, which have been obtained by solving Eqs. (7) and (13) with the collective multi-point density correlators $F^0_N((k_0), t)$ solved from Eq. (2) as inputs. Figure 2 shows the Percus–Yevick hard-sphere $F^0_{sc}(k_0, t)$ for several reduced packing fractions $c = (\varphi - \varphi^c)/\varphi^c$ under different MF closure levels $N$. For liquid states, i.e., when the packing fraction is below the corresponding GMCT critical point, $F^0_{sc}(k_0, t)$ decays from 1 to 0 (solid lines). However, for glass states with $\varphi \geq \varphi^c$, $F^0_{sc}(k_0, t)$ decays from 1 to the positive long-time limit $f^sc_0(k_0)$ (dashed lines). In the following, we will numerically show the scaling laws for these two states within GMCT.
1. Relaxation dynamics for liquid states

Let us first introduce some common properties of the liquid-state relaxation dynamics for all MF closure levels within GMCT. When the packing fraction is small and we are far from the critical point, the relaxation is governed by a relatively fast exponential decay. In contrast, when the packing fraction approaches the critical point, relaxation dynamics for all MF closure levels within GMCT.

The two exponents and are related to each other via

\[
\lambda = \frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}
\]

(26)

and

\[
y = \frac{1}{2a} + \frac{1}{2b},
\]

(27)

with \(0 < k < 1, 0 < a < 1/2, \) and \(b > 0\). Based on the obtained values for \(a\) and \(y\), the additional parameters have also been retrieved (see Table 1). Note that, in principle, one only needs one of the exponents to calculate the others. Importantly, we find that for all considered values of \(N\), all parameters are identical to the ones from the GMCT dynamics of the collective density correlators. This can also be strictly proved by expanding the SISF close to the critical point, see Ref. 18 for more details.) Thus, higher-order GMCT seems to maintain the equivalency of the critical exponents and \(\lambda\) between collective and tagged-particle motion, a result that is also obtained in standard MCT.

Now let us focus on the \(\beta\)-relaxation regime in more detail. Within MCT, to leading order in \(|\epsilon|\), there is a scaling law for \(F_0^\beta(k, t)\) near the plateau, i.e.,

\[
F_0^\beta(k, t) = f_0^\beta(k) + h^\beta(t)G(t).
\]

(28)

Here, \(G(t)\) is the so-called \(\beta\)-correlator (note that it is independent of the wavenumber \(k\)), which satisfies

\[
G(t) \sim \sqrt{|\epsilon|} g_\beta(t/\tau_\beta),
\]

(29)

and when \(\epsilon = 0^+\),

\[
G(t) \sim \begin{cases} t^a & \text{if } t < \tau_\beta, \\ t^b & \text{if } t > \tau_\beta. \end{cases}
\]

(30)

We find that these scaling laws are preserved within GMCT for all MF closure levels \(N \geq 2\) although the factors \(f_0^\beta(k), h^\beta(k), \) and the function \(g_\beta(t/\tau_\beta)\) become \(N\)-dependent. In order to demonstrate the respective scaling relations, we have first retrieved the critical amplitude \(h^\beta(k)\) for different \(N\). This has been done by simply taking two times \(t_1\) and \(t_2\) within the \(\beta\)-relaxation regime and using

\[
\frac{h^\beta(k)}{h^\beta(k^*')} = \frac{F_0^\beta(k, t_1) - F_0^\beta(k, t_2)}{F_0^\beta(k^*, t_1) - F_0^\beta(k^*, t_2)},
\]

(31)

which can be derived from Eq. (28). Figure 4 shows \(h^\beta(k)/h^\beta(k^*)\) with \(k^*d = 7.4\) for \(N = 2, 3, \) and 4. It can be seen that both the height of the peak of the scaled amplitude \(h^\beta(k)/h^\beta(k^*)\) and the wavenumber corresponding to the peak increase as \(N\) increases. We know from the weakly polydisperse hard-sphere simulations of Ref. 23 that the MCT-predicted wavenumber of the peak of \(h^\beta(k)/h^\beta(k^*)\) is already larger than the one from simulation data (see Fig. 11 in Ref. 23). The value of the peak is also overestimated by MCT. Therefore, for increasing closure level \(N\), more pronounced deviations from the simulation data seem to occur, and our current GMCT framework is manifestly unable to reach improved agreement.

We can explain the shift in the peak wavenumber by realizing that the \(\beta\)-relaxation regime corresponds to the caging effect and \(h^\beta(k)\) measures the decay of the SISF within this regime. We expect that the strongest decay occurs on length scales of the cage size, which would imply that higher-order GMCT predicts a smaller cage size. This will be confirmed when we study the MSD (see Fig. 11). Moreover, the fact that the peak shifts to larger wavenumbers also means that

![Figure 3. Relaxation times of the self-intermediate scattering functions \(F_0^\beta(k, t)\) at \(kd = 7.4\) for different GMCT MF closure levels. Squares are the numerical \(\alpha\)-relaxation times and circles are the numerical \(\beta\)-relaxation times. The solid lines are the fitted power-law curves \(\tau = \tau_0 |\epsilon|^{-\lambda}\). The dashed lines are the fitted power-law curves \(\tau_\beta = \tau_{0\beta} |\epsilon|^{-y}\). The \(\tau_0, \tau_{0\beta}, y\), and \(a\) are all \(N\)-dependent.](image-url)
$h'(k^*d = 7.4)$ takes on a relatively small value, which can explain why the height of the peak increases.

The scaling laws of Eqs. (28)–(30) in the $\beta$-relaxation regime can also be tested numerically from our GMCT SISF results for Percus–Yevick hard spheres. To test the power-law decay of Eq. (30), we set $\epsilon = -10^{-5} \sim 0^{-}$ to ensure a sufficiently close proximity to the critical point. Figure 5 shows the relative self-intermediate scattering functions $|p_n^0(k,t) - \tilde{f}_n^0(k)|/h'(k)$ at wavenumber $kd = 7.4$ for different closure levels $N$. All curves conform to power laws with exponents $-a$ and $b$ at the beginning and end of the $\beta$-relaxation regime, respectively, thus confirming the validity of Eq. (30).

Next, we test the scaling of $F_n^0(k,t)$ with the wavenumber $k$ [Eq. (28)] using the critical amplitudes of Fig. 4. Figure 6(a) shows the rescaled relative self-intermediate scattering functions $|F_n^0(k,t) - \tilde{f}_n^0(k)|/h'(k)$ at four different wavenumbers and $\epsilon = -10^{-3}$ for all considered MF closure levels. It can be seen that for a given closure level $N$ and reduced packing fraction $\epsilon$, all curves collapse onto one curve around $t = \tau_\beta$. This collapsed curve should then be proportional to $g_n(t/\tau_\beta)$ and corroborates the $k$-dependent scaling behavior of Eq. (28).

We complete our analysis of the $\beta$-relaxation regime by testing the scaling of $G(t)$ with $\epsilon$ [Eq. (29)]. Figure 6(b) shows the relative self-intermediate scattering functions $|F_n^0(k,t) - \tilde{f}_n^0(k)|$ normalized by $\sqrt{\epsilon}$ at wavenumber $kd = 7.4$. For each closure level $N$, all curves again collapse onto a single one near $t = \tau_\beta$. This demonstrates the scaling of $G(t)$ with the square-root of $|\epsilon|$, thus numerically confirming the validity of Eq. (29) within higher-order GMCT.
Let us now turn to the α-relaxation regime. We first seek to test the existence of a time–density (or time–temperature) superposition principle, which is well-established for standard MCT.\textsuperscript{12,32,38} Based on the equivalency of scaling laws for MCT and GMCT on the collective level,\textsuperscript{17,18} we hypothesize that this superposition principle also holds in the present case. Thus, up to order \( \sqrt{\epsilon} \), the self-GMCT-predicted α-relaxation of all \( F_0^k(k,t) \) should satisfy the relation

\[
F_0^k(k,t) = F_0^k(k,t/\tau_k).
\]  

(32)

This scaling law absorbs all explicit density (or temperature) dependence into the α-relaxation time scale \( \tau \) and therefore constitutes a time–density superposition. To substantiate our claim, we show the collapse of \( F_0^k(k,t) \) onto \( F_0^k(k,t/\tau) \) for two different wavenumbers \( kd = 7.4 \) [Fig. 7(a)] and \( kd = 13.0 \) [Fig. 7(b)] at several reduced packing fractions \( \epsilon \). For each closure level \( N \), all curves can be seen to collapse, which confirms the scaling law of Eq. (32) in the α-relaxation regime. It should, however, be noted that in addition to the different \( \tau \) for different \( N \), the master function \( F_0^k(k,t/\tau) \) also changes with \( N \). Thus, each new level in the GMCT hierarchy modifies the quantitative relaxation dynamics.

To complete the analysis of the α-relaxation regime for liquid states, we fit our results with the stretched-exponential Kohlrausch function,

\[
F_0^k(k,t) = A(k) \exp \left( -\frac{t}{\tau_k(k)} \right)^\beta(k),
\]  

(33)

for all considered MF closure levels. Figures 8(a) and 8(b) show the fit parameters \( \beta(k) \) and \( \tau_k(k) = \tau_k(k)/\tau_0(k' d = 7.4) \) at \( \epsilon = -10^{-3} \) [note that we do not show the fitted values of \( A(k) \) here since they are almost the same as \( f_0^k \) in Fig. 1]. We stress that the fit parameters are sensitive to the fitting range (especially for small wavenumbers), and hence, we have carefully selected the time domains such that at large wavenumbers, the fit results are very robust and exhibit only a weak dependence on the fit boundaries. It can be seen that as the closure level \( N \) increases, \( \beta(k) \) decreases. At the largest wavenumber \( k \) used in the numerical GMCT calculations, the value of \( \beta(k) \) for each level \( N \) is still larger than the corresponding value of \( b \). Moreover, the value of \( \beta(k) \) is also larger than the \( \beta(k) \) obtained from the fit of the collective intermediate scattering functions.\textsuperscript{17} We expect that in the limit of infinite wavenumber, \( \beta(k) \) obtained from both the SISF and ISF will converge to the respective value of \( b \) for a given \( N \).\textsuperscript{11} We mention that in simulations of weakly polydisperse hard spheres,\textsuperscript{7} the fitted \( \beta(k) \) is smaller than the one predicted by MCT (see the lower panel of Fig. 8 in Ref. 23). Interestingly, within GMCT, \( \beta(k) \) can be systematically lowered when using higher closure levels \( N \), which quantitatively improves its value and allows it to approach the simulation results.

By contrast, the MCT-predicted values for \( \tau_k(k) \) are already in reasonable agreement with the simulation data (see the lower panel of Fig. 7 in Ref. 23), and deviations appear mainly at small wavenumbers where \( \tau_k(k) \) is overestimated by MCT. Figure 8(b) demonstrates that by using higher-order GMCT, the deviations become slightly more severe as \( N \) increases. However, the qualitative form of the curves remains similar. To test if GMCT improves the prediction quantitatively, one would need to compare the unscaled relaxation time \( \tau_k(k) \), which has not been provided in Ref. 23.

2. Relaxation dynamics for glass states

In the glass phase, i.e., when the packing fraction is larger than the critical packing fraction \( (\epsilon > 0) \), the self-intermediate scattering functions \( F_0^k(k,t) \) fail to decay to zero and instead approach some finite positive value \( f_0^k \). These long-time limits \( f_0^k \) generally increase for increasing \( \epsilon \); more specifically, for all GMCT closure levels \( N \), they follow (to leading order in \( \epsilon \)) a scaling law similar to the one derived for MCT,\textsuperscript{17}

\[
f_0^k = f_0^k + C \sqrt{\epsilon} h_1(k).
\]  

(34)

FIG. 7. α-relaxation scaling laws for different MF closure levels. (a) Self-intermediate scattering functions for wavenumber \( kd = 7.4 \) at three different \( \epsilon \) values: \( \epsilon = -10^{-4} \) (solid lines), \( \epsilon = -10^{-3} \) (dashed lines), and \( \epsilon = -10^{-2} \) (dashed-dotted lines). Different colors correspond to different MF closure levels \( N \). For clarity, the lines are shifted horizontally by a factor of \( 10^{1-2} \). (b) Same as (a) except that \( kd = 13.0 \). For a given closure level \( N \) and \( \epsilon \), the \( \tau \) used here is the same as in (a), defined as \( F_0^k(kd = 7.4, \tau) = 0.1 \).
Here, $f_0^c(k)$ and $h^c(k)$ are the same functions introduced in Figs. 1 and 5, respectively, and $C$ is an $N$-dependent constant. Figure 9 shows the relative long-time limit of the SISF, $f_0^c(k) - f_0^g(k)$, as a function of $\sqrt{\epsilon}$ at two different wavenumbers. The linear relation at small $\sqrt{\epsilon}$ confirms the scaling with $\epsilon$ in Eq. (34).

Since no second decay step occurs in the glass state, there is only one relevant time scale $\tau^g_\beta$ that characterizes the $\beta$-relaxation regime. We have retrieved $\tau^g_\beta$, which can be defined as $F^g_0(k, \tau^g_\beta) - f_0^g(k) = 1.001(f_0^c(k) - f_0^g(k))$, numerically for each closure level $N$; the results are plotted in Fig. 10. Consistent with the $\beta$-relaxation time $\tau^g_\beta$ obtained in the liquid state, we observe that $\tau^g_\beta$ scales with the reduced packing fraction $\epsilon$ as $\tau^g_\beta \sim \epsilon^{-1/2a}$. We can thus use $\tau^g_\beta$ to characterize the $\beta$-relaxation regime for both the liquid and glass phases. The scaling laws of $F^g_0(k,t)$ in the $\beta$-relaxation regime of the glass state are also similar to the ones in the liquid state, i.e., Eqs. (28) and (29), except for a change $g_\alpha(t/\tau^g_\beta)$ to $g_\alpha(t/\tau^a_\beta)$. Since these scaling laws are preserved for all closure levels $N \geq 2$ in the liquid state, one can expect them to also hold in the glass state, which indeed we have verified numerically (data not shown here).

Summarizing, our results indicate that the scaling laws for the SISF from GMCT in both the liquid and glass states and in both the $\beta$- and $\alpha$-relaxation regimes are essentially the same as those predicted by MCT although the (exponent) parameters $a$, $b$, $y$, $\lambda$, $h^c(k)$, $\tau^g_\gamma$, and $\beta(k)$ change as the closure level $N$ increases. The values of the main exponents $a$, $b$, $\lambda$, and $y$ are also consistent with those obtained from the ISF for Percus–Yevick hard spheres. Therefore, the remarkably successful scaling laws in MCT are fully preserved in GMCT under generalized mean-field closures. We mention that...
the here discussed scaling laws for $F_0^s(k,t)$ are also applicable to higher-order density correlators $F_n^s(k_0,\{k_i\},t)$, similar to the case of the collective multi-point density correlators. This is because the mathematical structure of the GMCT equations is essentially identical for all levels of the hierarchy; the vertex only modifies the wavenumber-dependent exponents such as $h^s(k)$.

### C. Mean-squared displacement and the Stokes–Einstein relation

The MSD can be calculated via Eqs. (18) and (20) once $F_1^s(k_0,k_1,t)$ is known from GMCT. In Fig. 11, we show the obtained MSDs $\delta^2(t)$ (solid lines) at the critical point for all considered closure levels $N$ together with the corresponding memory functions $M_{\text{MSD}}(t)$ (dashed lines). In the long-time limit, $F_1^s(k_0,k_1,t)$ converges to some finite positive value so that $M_{\text{MSD}}(t)$ also remains positive and $\delta^2(t)$ becomes constant. We obtain the critical localization length $r_s$ from Eq. (24) (see the values of $r_s$ in Table I) and find that as $N$ increases, $r_s$ decreases, which means that the cage is smaller compared to the prediction from MCT. This is also consistent with the larger $f_{sc}^0(k)$ for higher $N$ shown in Fig. 1.

Figure 12 shows the tagged-particle MSDs in both the liquid and glass states at different reduced packing fractions $\epsilon$. It can be seen that for all considered closure levels $N$, the diffusion–localization transition exists: for packing fractions below the critical point, the particle always diffuses in the long-time limit with a diffusion coefficient $D_s$ as described by Eq. (21); for larger packing fractions $\phi \geq \phi_c$, the particle instead becomes localized. In Fig. 12, we find that the long-time diffusion coefficient follows a power law $D_s \sim |\epsilon|^{\gamma}$ for all GMCT levels, with the same fitted ($N$-dependent) exponent $\gamma$ as retrieved from the $\alpha$-relaxation time $\tau$ (see Fig. 3). We also plot the Stokes–Einstein relation, i.e., $D_s\tau$, in Fig. 13; it can be seen that the product $D_s\tau$ is almost constant for all packing fractions close to the critical point. This behavior is satisfied within GMCT for all MF closure levels $N$. Unfortunately, the empirical Stokes–Einstein violation for supercooled liquids is thus not captured by our current GMCT framework, analogous to the case in standard MCT.

![FIG. 11. The mean-squared displacement $\delta^2(t)$ (solid lines) and the associated memory functions $M_{\text{MSD}}(t)$ (dashed lines) at the critical packing fraction $\phi^c$ for Percus–Yevick hard spheres, obtained from GMCT for different MF closure levels $N$. The calculated localization lengths are $r_s = 0.0744, 0.0867, 0.0927$ for $N = 2, 3$ and 4, respectively.](image)

![FIG. 12. The mean-squared displacement $\delta^2(t)$ for Percus–Yevick hard spheres obtained from GMCT under MF closures (a) $N = 2$, (b) $N = 3$, and (c) $N = 4$. In all panels, the MSD is shown at $|\epsilon| = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}$ and $10^{-5}$ (from light to dark) for both liquid states (solid lines) and glass states (dashed lines).](image)
from the critical point, i.e., when $|\epsilon|$ is large, the Stokes–Einstein violation does appear and the deviation is larger as the level $N$ increases. This can be seen in the inset of Fig. 13 where we have plotted the relaxation times $\tau$ (as in Fig. 3). The solid lines are the fitted power-law curves $\tau = \tau_0|\epsilon|^\alpha$. The dashed lines are the fitted power-law curves $1/D' = |\epsilon|^\gamma/D_0$. The circles are $D'\tau$ scaled by the value of $D'\tau$ at $|\epsilon| = 10^{-1}$ and the dashed-dotted lines are guides to the eye. Inset: a linear-log plot of $D'\tau$ scaled by the value of $D'\tau$ at $|\epsilon| = 10^{-1}$.

To rationalize the preservation of the SER very close to the critical point within GMCT, let us take a closer look at Eqs. (20) and (22). Combining both equations gives

$$D' = D_0\left[1 + \int_0^\infty M_{\text{MSD}}(u)du\right]^{-1}$$

$$= D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty \rho^4 c^2(p) F_1(p, p, u) dpdu\right]^{-1}$$

$$= D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty dpp^4 c^2(p) \int_0^\infty F_1(p, p, u) du\right]^{-1}$$

$$= D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty dpp^4 c^2(p)\right]^{-1}$$

$$\times \left(\int_0^{\tau_0} F_1(p, p, u) + \int_0^{\tau_0} F_1(p, p, u) du\right)^{-1},$$

where, to split the time integral, we have introduced $\tau_0$ as the time scale at which the $\alpha$-relaxation starts. When we are close enough to the critical point, this time scale can be taken to satisfy $\tau_0/\tau \ll 1$. An inspection of both time integrals shows that the first is of the order $O(\tau_0)$ since in this range $F_1(p, p, u) \sim 1$, while the second one is at least of the order $O(\tau)$. This implies that we can neglect the first

$$D' \approx D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty dpp^4 c^2(p) \int_0^{\tau_0} F_1(p, p, u) du\right]^{-1}$$

$$= D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty dpp^4 c^2(p) \int_0^{\tau_0} F_1(p, p, u) du\right]^{-1}$$

$$= D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty dpp^4 c^2(p) \int_0^{\tau_0} F_1(p, p, v) dv\right]^{-1}$$

$$= D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty dpp^4 c^2(p) \int_0^{\tau_0} F_1(p, p, v) dv\right]^{-1}$$

$$= D_0\left[1 + \int_0^\infty \frac{\rho}{6\pi u^2} \int_0^\infty dpp^4 c^2(p) F_1(p, p, s = 0)\right]^{-1}$$

$$= D_0\left[1 + \tau D_0 MS\right]^{-1}$$

$$\approx \frac{1}{\tau M_{\text{SE}}} \cdot$$

Here, $M_{\text{SE}}$ is the relative memory function $M_{\text{SE}} = \frac{\rho}{6\pi} \int_0^\infty dpp^4 c^2(p) F_1(p, p, s = 0)$ with the Laplace transform $\hat{F_1}(p, p, s) = \int_0^\infty dt F_1(p, p, t) \exp(-st)$, and in the fourth and final step, we employ the approximations $\tau_0/\tau \ll 1$ and $\tau M_{\text{SE}} \gg 1$, respectively. The only additional relation we have used is the time–density superposition principle $F_1(p, p, t) = F_1(p, p, t/\tau)$, which can be derived and tested for all MF closure levels similar to the superposition principle for $F_0(k, t)$ in Eq. (32). Therefore, $D'\tau = 1/M_{\text{SE}}$ applies to all closure levels $N$ when approaching the critical point (although the precise value of $M_{\text{SE}}$ is $N$-dependent). In other words, as long as the time–density superposition of the $\alpha$-relaxation holds for $F_1(p, p, t)$, the SER cannot be violated.

The above finding seemingly constitutes a paradox for GMCT if we focus on states very close to the critical point: assuming that the time–density superposition holds for all wavenumbers, GMCT cannot account simultaneously for both the time–density superposition principle and the Stokes–Einstein violation. There are two possible ways to solve this paradox. One is by arguing that the time–density superposition principle is not fully satisfied for all wavenumbers, especially for small wavenumbers. In that case, the violation of the SER can emerge naturally. Hence, the problem shifts to the inaccurate prediction from GMCT for the dynamics of $F_1(k, k, t)$ at small wavenumbers $k$, which means the present GMCT framework is still largely applicable, but needs to be improved to provide a better prediction of the dynamics at small wavenumbers. In particular, such an improvement should effectively account for a decoupling between the dynamics at finite $k$ (where time–density or time–temperature superposition is typically observed) and the tagged-particle dynamics in the limit of $k \to 0$. We add that, of course, for packing fractions far away from the critical point, the SER could be violated trivially, consistent with the small violation observed in the inset of Fig. 13. The other possibility is that the framework of GMCT in itself still needs to be fundamentally and qualitatively improved to be able to capture the full phenomenology of glassy dynamics.
IV. CONCLUSION

In this work, we have developed a generalized mode-coupling theory for tagged-particle motion. Using the static structure factor $S(k)$ as the only material-dependent input, the theory predicts the microscopic relaxation dynamics of an arbitrary particle within a dense glass-forming system. The main new equations are the equations of motion for the tagged-particle multi-point density correlation functions [Eqs. (13)–(17)] and the equations for the mean-squared displacement [Eqs. (18)–(20)].

The newly developed theory has been applied to the Percus–Yevick hard-sphere system using different mean-field closures. We have comprehensively studied the dynamics of the self-intermediate scattering function near the liquid–glass transition in all its collective counterparts, the ISF. In particular, for a given packing fraction, increasing the mean-field closure level $N$ yields faster relaxation dynamics, while for a given reduced packing fraction, i.e., at the same relative distance to the critical point, the relaxation dynamics instead become slower as more levels are incorporated into the theory. The latter effect is also reflected in the increase of the self-non-ergodicity parameters $J_{\alpha}(k)$ at the critical point as the closure level $N$ increases. Therefore, the fact that increasing $N$ effectively enhances the non-linear feedback mechanism for the collective GMCT is also correct for the tagged-particle GMCT.

The asymptotic scaling laws of the SISF for both the liquid and glass states, which include the power laws governing the characteristic time scales, the time-wavenumber factorization in the $\beta$-relaxation regime, the time–density (or time–temperature) superposition principle, and the Kohlrausch stretching in the $\alpha$-relaxation regime, are all similar to those of the SISF within standard MCT at all GMCT MF closure levels considered. However, the corresponding parameters $a$, $b$, $y$, $\lambda$, $b'(k)$, $\tau_k(k)$, and $\beta(k)$ all explicitly depend on the closure level $N$. The main power-law exponent parameters $a$, $b$, $\lambda$, and $y$ agree with the corresponding values extracted from the predicted ISF within GMCT and have been shown to be closer to the empirical values with increasing $N$. The Kohlrausch stretching exponent $\beta(k)$, which converges toward $b$ in the long-wavenumber limit, has also been shown to reach better agreement with simulations as $N$ increases. The corresponding scaled $\alpha$-relaxation time $\tau_\alpha^*(k)$ instead remains qualitatively similar to the MCT result upon increasing the GMCT closure level although we expect the actual relaxation time $\tau_k(k)$ to be quantitatively improved. Interestingly, by contrast, the GMCT-predicted critical amplitude $b'(k)$ seems to increasingly deviate from the simulation data, with the predicted peak value shifting toward larger wavenumbers. This may be linked to the smaller predicted cage length $r_c$ at higher closure levels. Overall, we conclude that the higher-order GMCT framework for tagged-particle motion inherits virtually all qualitative features of standard MCT; however, all numerical predictions for the dynamics change quantitatively upon increasing the closure level, and for most properties studied here, we find systematic numerical improvement.

We mention that an additional advantage of the present framework is that it allows for the predictions of tagged-particle multi-point density correlation functions. Such correlation functions are related to, e.g., the susceptibility and the dynamical correlation length and can be calculated and compared to those measured from simulation and experiments. Work along these lines is already in progress and will be reported on in future studies.

Unfortunately, our present theory cannot predict the Stokes–Einstein violation for supercooled liquids. In fact, within GMCT, we have proved that the time–density (or time–temperature) superposition principle and the Stokes–Einstein violation are in conflict with each other and that the current theory is unable to account for both phenomena simultaneously—regardless of the closure level. Recently, the Stochastic Beta Relaxation (SBR) theory has successfully explained the Stokes–Einstein violation qualitatively by including long-wavelength fluctuations in the MCT scaling laws. We mention that SBR is an approach that can possibly be combined with GMCT because the scaling laws from GMCT are qualitatively similar (although quantitatively different) to those obtained in MCT and can thus constitute an interesting follow-up step. Alternatively, to develop a fully first-principles-based theory, qualitative improvements of the framework, e.g., by including the previously neglected off-diagonal terms of the higher-order correlators in the memory function or by changing the set of slow variables in the Zwanzig–Mori projection operator, are needed to adequately capture Stokes–Einstein violation. More generally, such additional effort is likely necessary to fully account for the emergence of dynamical heterogeneity, in particular to describe hopping and facilitation effects or activated dynamical processes on a strictly first-principles basis.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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