

High-Order Mode-Coupling Theory for the Colloidal Glass Transition

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A theoretical approach is developed to derive a hierarchy of mode-coupling equations for the dynamics of concentrated colloidal suspensions, which improves the prediction of the colloidal glass transition. Our derivation is based on a matrix formalism for stochastic dynamics and the resulting recursive expressions for irreducible memory functions. The 1st order truncation of the generalized mode-coupling closure recovers mode-coupling theory, whereas its 2nd and 3rd order truncations provide corrections. The predictions of the transition volume fraction and Debye-Waller parameter for the hard-sphere colloidal system improve with the increasing mode-coupling order and compare favorably with experimental measurements.

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The key predictions of mode-coupling theory (MCT) are the ergodic-to-nonergodic transition and associated dynamic scaling [1–3]. These predictions have been supported by numerical simulations of simple liquids and scattering measurements of colloidal suspensions, which are often described as a many-body Brownian system with pairwise interactions. Because of its simplicity and the wealth of experimental investigations, an assembly of spherical colloidal particles has been an ideal system for demonstrating dynamic slowdown and the glass transition both experimentally and theoretically [4].

In the standard projection operator formalism, the coherent intermediate scattering function $F_k(t)$ is described by the generalized Langevin equation with a memory kernel, which is a bilinear density correlation function or four-point correlation function. The Gaussian factorization scheme decomposes the bilinear memory kernel into a product of two linear correlation functions. The simple closure gives a nonlinear equation for the density correlation, which describes the dynamic feedback effect between the strength of density fluctuations and the friction applied to these fluctuations [3]. The feedback mechanism explains the formation of local cages formed by neighboring particles as the density (volume fraction ϕ) increases. The relaxation predicted by MCT consists of the β process and α process, corresponding to the formation and the breakup of cages, respectively. At a critical volume fraction, the colloid particles are permanently trapped in local cages and $F_k(t)$ has a nonzero long-time plateau, $\lim_{t \rightarrow \infty} F_k(t) = f_k S_k$, where S_k is the structure factor, and f_k is known as the nonergodic parameter or the Debye-Waller parameter. The ergodic-to-nonergodic transition predicted by MCT is often identified as the ideal glass transition and has been supported by experiments and computer simulations [5–7].

The enormous success of MCT has inspired theorists to improve the accuracy of its predictions and extend the range of its applicability. However, such theoretical improvements prove to be challenging. The mean-field nature of the ideal MCT overestimates the strength of the non-

linear feedback and does not fully account for the hopping events which are more frequent for finite size cages [8,9]. These hopping events destroy the plateau predicted by MCT and eventually restore ergodicity. As a result, the MCT transition volume fraction for a hard-sphere solution, $\phi^{(1)} = 0.525$, is smaller than the experimental transition point at $\phi^E \approx 0.58$ by 10% [3,5]. To improve MCT predictions, we need to systematically incorporate multiparticle correlations into the mean-field approach. Götze and his coworkers proposed extensions to MCT, but the detailed calculations are demanding and may require additional input [10]. Tokuyama *et al.* captured the slow relaxation and dynamic heterogeneities in supercooled colloidal suspensions using a pair of coupled diffusion equations, which were derived under different assumptions from those of MCT [11]. Szamel proposed an extension to MCT based on a high-order factorization scheme and improved the predictions of the colloidal glass transition point for the hard-sphere system [12]. Although his scheme is an important extension beyond MCT, the derivation involves projection operators which are not easy to compute for higher order. Recently, MCT was formulated without using the projection operator technique [13,14]. Along this line, we derived hydrodynamic equations for four-point correlation functions, and were able to relate non-Gaussian effects in bilinear density fluctuations to the nonexponential decay in linear density correlation [14].

The goal of this Letter is to systematically derive high-order mode-coupling equations and improve the prediction of the colloidal glass transition density. Our calculations are based on a matrix formalism of stochastic dynamics and the resulting recursive expressions. To begin, we use the linear variable A_1 and its products $A_1 A_1$, $A_1 A_1 A_1$, etc., to construct an orthogonal basis set $\{A_i\}$ normalized by $\mathbb{K}_{i,j} \equiv \langle A_i^* A_j \rangle = \langle A_i^* A_i \rangle \delta_{i,j}$, by the Gram-Schmidt method [15,16]. The normalized correlation function for A_i is defined by $C_i(t) \equiv \langle A_i^* \exp(\mathbf{D}t) A_i \rangle \mathbb{K}_i^{-1}$ or equivalently $\hat{C}_i(z) \equiv \langle A_i^* (z\mathbb{1} - \mathbf{D})^{(-1)} A_i \rangle \mathbb{K}_i^{-1}$ in the Laplace domain, where \mathbf{D} is the propagation operator. The inversion of the

$z\mathbb{1} - \mathbf{D}$ matrix is simplified by sorting the basis set elements of $\{A_i\}$ into the block tridiagonal form $\mathbb{D}_{\mu,\nu} \equiv \langle A_\mu^* \mathbf{D} A_\nu \rangle = \mathbb{D}_{\mu,\nu} \delta_{\mu,\nu} + \mathbb{D}_{\mu,\mu\pm 1} \delta_{\nu,\mu\pm 1}$, which defines the coupling scheme represented by a coupling tree in

$$\left\{ \begin{array}{l} n_1(\vec{k}) = n_{\vec{k}} \\ n_2(\vec{k}_1, \vec{k}_2) = n_{\vec{k}_1} n_{\vec{k}_2} - \langle n_{\vec{k}_1} n_{\vec{k}_2} n_{\vec{k}}^* \rangle N^{-1} S_k^{-1} n_{\vec{k}} \\ n_3(\vec{q}_1, \vec{q}_2, \vec{q}_3) = n_{\vec{q}_1} n_{\vec{q}_2} n_{\vec{q}_3} - \langle n_{\vec{q}_1} n_{\vec{q}_2} n_{\vec{q}_3} n_{\vec{k}}^* \rangle N^{-1} S_k^{-1} n_{\vec{k}} - \langle n_{\vec{q}_1} n_{\vec{q}_2} n_{\vec{q}_3} n_2^*(\vec{k}_1, \vec{k}_2) \rangle * \mathbb{K}_{22}^{-1}(\vec{k}_1, \vec{k}_2; \vec{k}_1', \vec{k}_2') * n_2(\vec{k}_1', \vec{k}_2') \end{array} \right. \quad (1)$$

where $\mathbb{K}_{i,j}$ is the susceptibility matrix, $\mathbb{K}_{i,j} \equiv \langle n_i n_j^* \rangle = \mathbb{K}_{i,i} \delta_{i,j}$, * in $(X * Y)$ indicates the summation over the repeated indices of the wave vectors in quantities X and Y , and the time dependence for each mode is omitted for simplicity. To avoid overcounting, the sequences of wave vectors are ordered as $(\vec{k}_1 > \vec{k}_2)$ and $(\vec{q}_1 > \vec{q}_2 > \vec{q}_3)$. The translational invariance requires the summation of the wave vector for each mode be the same, $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = \vec{k}_1 + \vec{k}_2 = \vec{k}$. The Smoluchowski operator for the N -body colloidal system is $\mathbf{D} = D_0 \sum_i \partial / \partial \vec{r}_i [\partial / \partial \vec{r}_i - \beta \vec{F}_i]$, where D_0 is the diffusion coefficient of a noninteracting particle and \vec{F}_i is the force applied to the particle. According to the N -ordering approximation scheme [16], the resulting kinetic matrix $\mathbb{D}_{i,j} \equiv \langle n_i \mathbf{D} n_j^* \rangle$ is block tridiagonal in the large N limit, $\mathbb{D}_{i,j} = \mathbb{D}_{i,i} \delta_{i,j} + \mathbb{D}_{i,i\pm 1} \delta_{j,i\pm 1}$. The natural choice for constructing mode-coupling approximations is a set of irreducible functions, which decay slower than the corresponding correlation functions. In the Laplace domain, the irreducible correlation functions are related to each other by the recursive expression [17]

$$\begin{aligned} \hat{\mathbb{C}}_i^{ir}(z) &\equiv [z\mathbb{1} + \Omega_i^{ir} - \hat{\mathbb{M}}_i^{ir}(z)]^{-1} \\ &= \{z\mathbb{1} + \Omega_i^{ir} [\Omega_i^{ir} + \hat{\mathbb{M}}_i^{ir}(z)]^{-1} \Omega_i^{ir}\}^{-1}, \end{aligned} \quad (2)$$

where the i th order irreducible eigenfrequency is

$$\begin{aligned} \Omega_i^{ir} &= \Omega_i - \mathbb{D}_{i,i-1} \mathbb{K}_{i-1,i-1}^{-1} \Omega_{i-1}^{ir} \mathbb{D}_{i-1,i} \mathbb{K}_{i,i}^{-1} \\ &= \Omega_i - \mathbb{D}_{i,i-1} \mathbb{K}_{i-1,i-1}^{-1} [\Omega_{i-1} \\ &\quad - \mathbb{D}_{i-1,i-2} \mathbb{K}_{i-2,i-2}^{-1} (\dots) \mathbb{D}_{i-2,i-1} \mathbb{K}_{i-1,i-1}^{-1}] \\ &\quad \times \mathbb{D}_{i-1,i} \mathbb{K}_{i,i}^{-1} \end{aligned} \quad (3)$$

with $\Omega_i \equiv -\mathbb{D}_{i,i} \mathbb{K}_i^{-1}$, and the i th order irreducible memory kernel is

$$\hat{\mathbb{M}}_i^{ir}(z) = \mathbb{D}_{i,i+1} \mathbb{K}_{i+1,i+1}^{-1} \hat{\mathbb{C}}_{i+1}^{ir}(z) \mathbb{D}_{i+1,i} \mathbb{K}_{i,i}^{-1}. \quad (4)$$

These expressions are the basis for deriving dynamic equations and applying mode-coupling closures. In comparison with the standard projection approach, our derivation is transparent and easy to generalize. Instead of projecting onto nonlinear modes, the matrix structure introduces a natural framework of generating the hierarchy coupling scheme. The recursive relations explain the need for irreducible functions and provide a simpler tool than irreducible operators. In an earlier application to the East model,

Ref. [17]. For colloidal systems, the relevant linear variable is the collective density, $n_{\vec{k}}(t) = \sum_{l=1}^N \exp[-i\vec{k}\vec{r}_l(t)]$, where N is the number of colloid particles, \vec{k} is the wave vector, and $\vec{r}_l(t)$ is the position of particle l at time t . The complete basis set is

we established a connection between Andersen's diagrammatic expansion and our mode-coupling tree and derived several high-order corrections to the MCT approximations [17,18].

In the following, we use the matrix formalism to derive the MCT memory kernel and its 2nd order/3rd order extensions. The 1st order normalized correlation function is related to the coherent intermediate scattering function by $\mathbb{C}_1(\vec{k}; t) = F_k(t)/S_k$. From Eqs. (2)–(4), $\hat{\mathbb{C}}_1(\vec{k}; z)$ is written as

$$\begin{aligned} \hat{\mathbb{C}}_1(\vec{k}; z) &= \left\langle n_1(\vec{k}) \frac{1}{z - \mathbf{D}} n_1^*(\vec{k}) \right\rangle \\ &= \left[z + \frac{\Omega_1(\vec{k})}{1 + \Omega_1^{-1}(\vec{k}) \hat{\mathbb{M}}_1^{ir}(\vec{k}; z)} \right]^{-1}, \end{aligned} \quad (5)$$

where $\Omega_1(\vec{k})$ is the 1st order eigenfrequency, $\Omega_1(\vec{k}) = \omega_k \equiv k^2/S_k$, and $\hat{\mathbb{M}}_1^{ir}(\vec{k}; z)$ is the 1st order irreducible memory kernel, $\hat{\mathbb{M}}_1^{ir}(\vec{k}; z) = \mathbb{D}_{1,2} * \mathbb{K}_{2,2}^{-1} * \hat{\mathbb{C}}_2^{ir}(z) * \mathbb{D}_{2,1} * \mathbb{K}_{1,1}^{-1}$. The diagonal approximation [16] simplifies $\hat{\mathbb{M}}_1^{ir}(\vec{k}; z)$ to

$$\mathbb{M}_1^{ir}(\vec{k}; t) = \sum_{\vec{k}_1 > \vec{k}_2} \delta_{\vec{k}_1 + \vec{k}_2, \vec{k}} \frac{|\mathbb{D}_{1,2}(\vec{k}; \vec{k}_1, \vec{k}_2)|^2 \mathbb{C}_2^{ir}(\vec{k}_1, \vec{k}_2; t)}{\mathbb{K}_{22}(\vec{k}_1, \vec{k}_2) N S_k}, \quad (6)$$

which is a general equation to evaluate viscosity. Applying the Gaussian factorization scheme $\mathbb{C}_2^{ir}(\vec{k}_1, \vec{k}_2; t) = \mathbb{C}_1(\vec{k}_1; t) \mathbb{C}_1(\vec{k}_2; t)$ to Eq. (6), recovers the standard mode-coupling memory kernel

$$\begin{aligned} \mathbb{M}_1^{ir}(\vec{k}; t) &= \sum_{\vec{k}_1 > \vec{k}_2} \frac{n_0^2 S_{k_1} S_{k_2}}{N S_k} [(\vec{k} \cdot \vec{k}_1) c_{k_1} \\ &\quad + (\vec{k} \cdot \vec{k}_2) c_{k_2}]^2 \mathbb{C}_1(\vec{k}_1; t) \mathbb{C}_1(\vec{k}_2; t), \end{aligned} \quad (7)$$

where the Kirkwood approximation is used for the three-particle distribution function in $\mathbb{D}_{1,2}(\vec{k}; \vec{k}_1, \vec{k}_2)$. The original MCT was derived from Newtonian dynamics, whereas colloid particles follow Brownian dynamics. A key difference between the two dynamics is the role of irreducible functions in the long-time behavior of stochastic systems [17,19]. As demonstrated here and shown by several authors earlier, the standard MCT memory function can be recovered when Gaussian factorization is applied to the 1st

order irreducible memory kernel instead of the memory kernel. Although the short time correlations are different for the two dynamics, MCT predicts the same glass transition point and f_k value for colloids and liquids with the same pairwise interaction potential. Experimentally, the MCT predictions are found to be more reliable for Brownian dynamics than for Newtonian dynamics.

As demonstrated in earlier work [3], applying the factorization scheme to high-order irreducible memory kernels improves the prediction of MCT. We evaluate $\hat{\mathbb{C}}_2^{ir}(z)$ using the same procedure as for $\hat{\mathbb{C}}_1^{ir}(z)$. From Eqs. (2)–(4), we obtain the diagonal four-point irreducible correlation function,

$$\hat{\mathbb{C}}_2^{ir}(\vec{k}_1, \vec{k}_2; z) = \left[z + \frac{\Omega_2^{ir}(\vec{k}_1, \vec{k}_2)}{1 + (\Omega_2^{ir}(\vec{k}_1, \vec{k}_2))^{-1} \hat{\mathbb{M}}_2^{ir}(\vec{k}_1, \vec{k}_2; z)} \right]^{-1}, \quad (8)$$

where the 2nd order irreducible eigenfrequency is

$$\begin{aligned} \Omega_2^{ir}(\vec{k}_1, \vec{k}_2) &= \Omega_2(\vec{k}_1, \vec{k}_2) - \mathbb{D}_{2,1}(NS_k)^{-1} \Omega_1 \mathbb{D}_{1,2} \mathbb{K}_{2,2}^{-1} \\ &\approx \omega_{k_1} + \omega_{k_2}, \end{aligned} \quad (9)$$

and the 2nd order irreducible memory kernel is $\mathbb{M}_2^{ir}(t) = \mathbb{D}_{2,3} * \mathbb{K}_{33}^{-1} * \mathbb{C}_3^{ir}(t) * \mathbb{D}_{3,2} * \mathbb{K}_{22}^{-1}$. The combined use of the diagonal approximation, the Kirkwood approximation, and the Gaussian factorization scheme leads to a new closure,

$$\hat{\mathbb{C}}_3^{ir}(\vec{q}_1, \vec{q}_2, \vec{q}_3; z) = \left[z + \frac{\Omega_3^{ir}(\vec{q}_1, \vec{q}_2, \vec{q}_3)}{1 + (\Omega_3^{ir}(\vec{q}_1, \vec{q}_2, \vec{q}_3))^{-1} \hat{\mathbb{M}}_3^{ir}(\vec{q}_1, \vec{q}_2, \vec{q}_3; z)} \right]^{-1}, \quad (12)$$

where $\Omega_3^{ir}(\vec{q}_1, \vec{q}_2, \vec{q}_3) = \omega_{q_1} + \omega_{q_2} + \omega_{q_3}$ and the 3rd order irreducible memory kernel is

$$\begin{aligned} \mathbb{M}_3^{ir}(\vec{q}_1, \vec{q}_2, \vec{q}_3; t) &\approx \mathbb{M}_1^{ir}(\vec{q}_1; t) \mathbb{C}_1(\vec{q}_2; t) \mathbb{C}_1(\vec{q}_3; t) \\ &+ \mathbb{M}_1^{ir}(\vec{q}_2; t) \mathbb{C}_1(\vec{q}_1; t) \mathbb{C}_1(\vec{q}_3; t) \\ &+ \mathbb{M}_1^{ir}(\vec{q}_3; t) \mathbb{C}_1(\vec{q}_1; t) \mathbb{C}_1(\vec{q}_2; t). \end{aligned} \quad (13)$$

By extrapolating Eqs. (11) and (13) to higher orders, we obtain

$$\mathbb{M}_i^{ir}(\{\vec{k}_l\}; t) \approx \sum_{l=1}^i \mathbb{M}_1^{ir}(k_l; t) \prod_{j=1(\neq l)}^i \mathbb{C}_1(k_j; t), \quad (14)$$

which can be used as a generalized MCT closure. This compact form decomposes the high-order irreducible memory kernel into terms consisting of the 1st order functions and can be viewed as an simplified factorization scheme for multipoint memory functions. Compared to the full expression, Eq. (14) achieves similar convergence at reduced computational cost.

The glass transition point in colloids is determined by the appearance of a nonzero long-time plateau in $F_k(t)$. To test the accuracy of our prediction of the colloidal glass transition, we numerically compute the Debye-Waller parameters, $f_k = \lim_{t \rightarrow \infty} \mathbb{C}_1(k; t)$, for the hard-sphere system.

$$\begin{aligned} \mathbb{M}_2^{ir}(t) &= \sum_{l_1, p_1, \{\vec{q}_i\}} \frac{n_0^2 S_{q_{p_2}} S_{q_{p_3}}}{NS_{k_{l_1}}} [(\vec{k}_{l_2} \cdot \vec{q}_{p_2}) c_{q_{p_2}} \\ &+ (\vec{k}_{l_2} \cdot \vec{q}_{p_3}) c_{q_{p_3}}]^2 \delta_{\vec{q}_{p_1}, \vec{k}_{l_1}} \mathbb{C}_1(q_1; t) \mathbb{C}_1(q_2; t) \mathbb{C}_1(q_3; t), \end{aligned} \quad (10)$$

where $l_1, l_2 = 1, 2, p_1, p_2, p_3 = 1, 2, 3$, and the summation over $\{\vec{q}_i\}$ is constrained by $(\vec{q}_1 > \vec{q}_2 > \vec{q}_3)$ and $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = \vec{k}_1 + \vec{k}_2 = \vec{k}$. The multiple summations over the wave vectors $\{\vec{q}_i\}$ in Eq. (10) quickly increase the difficulty of numerical calculations. To avoid this difficulty, we substitute Eq. (7) into Eq. (10) and obtain a simplified expression

$$\mathbb{M}_2^{ir}(\vec{k}_1, \vec{k}_2; t) \approx \mathbb{M}_1^{ir}(\vec{k}_1; t) \mathbb{C}_1(\vec{k}_2; t) + \mathbb{M}_1^{ir}(\vec{k}_2; t) \mathbb{C}_1(\vec{k}_1; t). \quad (11)$$

The underestimation due to the mixing of the 1st order and 2nd order expressions in Eq. (11) compensates for the overestimation of the dynamic feedback by the MC closures in Eqs. (7) and (10). We also expect the difference between the two expressions becomes negligible as the mode-coupling order increases.

The derivation of the 3rd order MCT equation is straightforward but tedious. Here we present the final result for the diagonal six-point irreducible correlation function using Eqs. (2)–(4) and the same approximations for $\hat{\mathbb{C}}_2^{ir}(z)$,

The long-time limit of Eq. (5) leads to $\lim_{t \rightarrow \infty} \mathbb{M}_1(k; t) = \omega_k^2 f_k / (1 - f_k)$. The i th order self-consistent equation of f_k are derived by substituting the asymptotic limits of $\mathbb{C}_1(k; t)$ and $\mathbb{M}_1^{ir}(k; t)$ into the recursive expression for $\mathbb{C}_i^{ir}(t)$ in Eqs. (2)–(4) and the MC closure for $\mathbb{M}_i^{ir}(t)$ in Eq. (14). For example, the closure for $\mathbb{M}_2^{ir}(t)$ in Eq. (11) gives the 2nd order MCT prediction of f_k ,

$$\begin{aligned} \frac{f_k}{1 - f_k} &= \frac{S_k}{192\pi\phi} \int_0^\infty dk_1 \int_{|k-k_1|}^{k+k_1} dk_2 \frac{k_1 k_2}{k^5} [(k^2 + k_1^2 - k_2^2) n c_{k_1} \\ &+ (k^2 + k_2^2 - k_1^2) n c_{k_2}]^2 \\ &\times \frac{S_{k_1} S_{k_2} f_{k_1} f_{k_2}}{f_{k_1} f_{k_2} + \frac{(\omega_{k_1} + \omega_{k_2})^2}{\omega_{k_1}^2 (1 - f_{k_1})^{-1} + \omega_{k_2}^2 (1 - f_{k_2})^{-1}}}, \end{aligned} \quad (15)$$

which recovers the standard MCT expression in the limit of $f_k \rightarrow 1$. The derivation of the 3rd order equation is straightforward and is not included due to length restrictions. Following the numerical method in Ref. [7], we discretize the integration in Eq. (15) with the grid resolution of $d\Delta k = 0.4$ in the range of $0.2 \leq k_1 d, k_2 d \leq 39.8$ and $|k - k_1| + 0.2d^{-1} \leq k_2 \leq k + k_1 - 0.2d^{-1}$, where d is the diameter of the colloid particle. The numerical solution of $f(k)$ is zero at low density and jumps to a

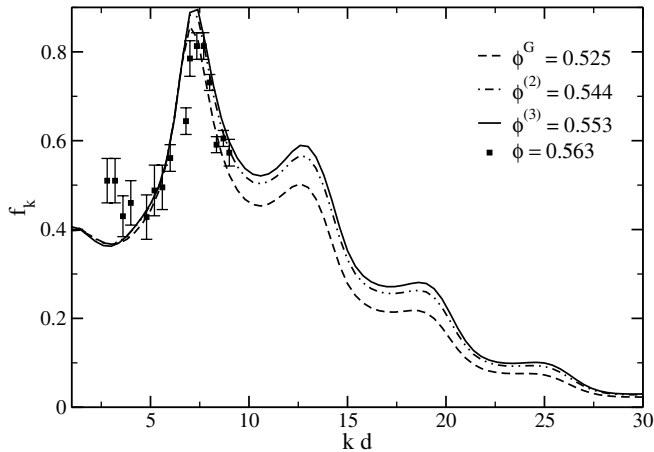


FIG. 1. Debye-Waller parameters at the ergodic-to-nonergodic transition point. The length unit is the diameter of colloidal particles. The dashed line is from Götze's idealized MCT, $\phi^{(1)} = 0.525$. The dot-dashed line is from our 2nd order MCT, $\phi^{(2)} = 0.545$. The solid line is from our 3rd order MCT, $\phi^{(3)} = 0.552$. The symbols are the experimental data by van Meegen *et al.* [5].

nontrivial solution at the ergodic-to-nonergodic transition point. The volume fractions at the predicted transition points are: $\phi^{(1)} = 0.525$ from the standard MCT, $\phi^{(2)} = 0.545$ from the 2nd order solution, and $\phi^{(3)} = 0.552$ from the 3rd order solution. These predictions converge with increasing mode-coupling order and compare favorably with the observed colloidal glass transition at $\phi^E \approx 0.58$.

The Debye-Waller functions at the predicted transition points are plotted in Fig. 1 along with the experimental data [5] at $\phi = 0.563$. The experimentally measured f_k curves depend strongly on the volume fraction and would not yield a meaningful comparison with the MCT predictions if the same volume fraction is used, because the predicted transition point is different. Instead, the comparison should be calibrated by the distance to the transition point $[\phi - \phi^{(i)}]/\phi^{(i)}$ so that the observed and predicted dynamics scale accordingly. As shown in Fig. 1, the predicted f_k functions at the MCT transition points agree well with the experimental f_k at the colloidal glass transition point. This observation supports the use of the distance to the transition point as the scaling parameter instead of the density or temperature. The relatively small variations of f_k with increasing mode-coupling order indicate that MCT is a convergent theory and can be systematically improved.

In conclusion, the matrix formalism allows us to systematically derive high-order generalizations of Götze's MCT and provides convergent predictions of the Debye-Waller parameter and the nonergodic transition density. Further developments of this formalism will lead to several possible applications, including dynamic scaling relations [7], non-Gaussian effects in bilinear modes [14,20–22], and the phase diagrams for the colloidal systems with the square-well potential and the Yukawa potential [23–25].

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