A Diagrammatic Kinetic Theory for a Lattice Model of a Liquid: II. Comparison of Theory and Simulation Results

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We compare the predictions of the mean field, the two site multiple scattering, and the simple mode coupling approximation developed in the previous paper for the dynamics of a tagged particle in an excluded volume lattice gas with the results of computer simulations. The tagged particle has a transition rate of $\gamma$ while the background particles have transition rates of $\alpha\gamma$. We consider the tracer diffusion coefficient and the incoherent intermediate scattering function (IISF) for low, intermediate and high concentrations of particles and for simple square and cubic lattices. In general, the approximate kinetic theories are more accurate in predicting simulations results at low concentrations, high dimensions and large $\alpha$. For the tracer diffusion coefficient, the mean field approximation is the least accurate, the two site multiple scattering approximation is more accurate, and the simple mode coupling approximation is the most accurate; all three approximate theories overestimate the simulation results. For the IISF, the mean field approximation is quantitatively accurate in the limit of small concentration and large $\alpha$ but in general decays too quickly. The two site multiple scattering approximation is quantitatively accurate at low and intermediate concentrations for large wave vectors; it is always more accurate than the mean field approximation and always decays more quickly than the simulation results. The simple mode coupling approximation is the most accurate of the three approximations in most cases and especially so for small wave vectors, high concentration and small $\alpha$; unfortunately, its predictions are not quantitatively accurate in these highly non mean field regimes. We discuss the implications of these results for developing diagrammatic kinetic theories.

I. INTRODUCTION

In the previous paper, we used a diagrammatic formalism to develop a series of approximate kinetic theories for the dynamics of a tagged particle in an excluded volume lattice gas. By making approximations to the diagrammatic series for the irreducible memory function, we derived the mean field approximation (MFA), the two site multiple scattering approximation (TMSA), and the simple mode coupling approximation (SMCA). Here, we compare the predictions of these kinetic theories for the tracer diffusion coefficient and the incoherent intermediate scattering function (IISF) with the results of computer simulations.

For this excluded volume lattice gas, particles occupy sites on a lattice, but two particles are not allowed to occupy the same site; otherwise, there are no interactions between the particles. Each particle has a species dependent transition rate to each unoccupied nearest neighbor site, and the stochastic dynamics governing the system satisfy the detailed balance condition. To describe the dynamics of a tagged particle, we consider a two component system in which one component is present in trace amounts. Particles of the trace and dominant component have transition rates of $\gamma$ and $\alpha\gamma$ respectively, where $\gamma^{-1}$ has units of time. This corresponds to a system with one tagged particle and background particles that can have either the same ($\alpha = 1$) or a different ($\alpha \neq 1$) transition rate.

The important physics of the dynamics of the tagged particle is the backwards correlation effect. If the tagged particle makes a transition to a neighboring site, the particle has a higher probability of making its next transition back to the original site since it is originally unoccupied. After a time interval, the probability of finding a background particle at this original site returns to its mean value, and this original site is no longer different from the other sites surrounding the tagged particle. The backwards correlation effect is larger at higher particle concentrations, lower dimensions, and small values of $\alpha$, and it makes predicting the dynamics of the trace particle challenging. In the opposite regimes of low particle concentration, higher dimensions and large $\alpha$, the backwards correlation effect is minimal, and we expect that a mean field description of the dynamics is accurate.

A comprehensive summary of both the theoretical and computational work on the excluded volume lattice gas was given by Kehr and Binder.\textsuperscript{1} The primary quantity of interest is the correlation factor $f(c, \alpha)$, the ratio of the diffusion coefficient of a tagged particle to the mean field approximation for this quantity. Here, $c$ is the concentration of particles while $\alpha$ is the ratio of the dominant transition rate to the trace transition rate. (We use this notation throughout the paper.) Of the previous theoretical work, the work of Nakazato and Kitahara\textsuperscript{2} and of van Beijeren and Kutner\textsuperscript{3} focused on approximate calculations of the correlation factor while the theories of Fedders and Sankey\textsuperscript{4–7} and of Tahir-Kheli and Elliott\textsuperscript{8}
It is conventional to define the correlation factor as the function.

In Section II, we summarize the predictions of the three kinetic theories in the previous paper. Section III gives the details of the computer simulations. In Section IV, we compare the results of the three kinetic theories with simulations, and we discuss the implications of these results in Section V.

II. PREDICTIONS OF KINETIC THEORIES

The most simple kinetic theory is the mean field approximation (MFA), the set of diagrams for the response function with only vertices containing one left point and one right point. The IISF is

\[ C_s(k; t) = \exp \left( -\gamma (1 - c) M_d(k) t \right) \quad (1) \]

where

\[ M_d(k) = 2d - \sum_n e^{ik \cdot n} = 2 \sum_{i=1}^d \left( 1 - \cos k_i \right). \]

\( n \) is the vector between two nearest neighbor sites on the lattice, and \( d \) is the dimension of the lattice. We obtain the tracer diffusion coefficient \( D_{tr}(c, \alpha) \) from the behavior of \( C_s \) for long times and small \( |k| \). Then the mean field approximation predicts \( D_{tr}(c, \alpha) = \gamma (1 - c) \).

It is conventional to define the correlation factor as the ratio of the tracer diffusion coefficient to the mean field result.\(^1\)

\[ f(c, \alpha) = \frac{D_{tr}(c, \alpha)}{\gamma (1 - c)}. \]

Thus, the mean field approximation gives \( f(c, \alpha) = 1 \) for all \( c \) and \( \alpha \). The mean field prediction for the dynamics of a trace particle is equivalent to the exact dynamics of a single particle on an otherwise empty lattice that performs a random walk with a reduced transition rate \( \gamma (1 - c) \).

We derived the two site multiple scattering approximation (TSMSA) from the time ordered series for the response function. In an approximate manner, it describes the motion of a trace particle as a correlated random walk rather than an uncorrelated random walk. In particular, it describes the exact dynamics of a trace particle on two nearest neighbor sites, or that the trace particle has a transition rate of zero or \( \gamma \) to the other neighboring site if a background particle does or does not occupy this site respectively. The dynamics of the trace and background particle to the other surrounding sites are approximated in a mean field manner. The Fourier Laplace transform of the self-correlation function in this approximation is

\[ \hat{C}_s(k; s) = \frac{s + A}{s^2 + sB + C} \]

where \( A = \gamma \left( l(1 - c + \alpha) + 2c \right), B = \gamma \left( l(1 - c + \alpha) + 2c \right) + \gamma (1 - c)M_d(k), C = \gamma^2 l(1 - c)(1 - c + \alpha)M_d(k) \), and \( l = 2d - 1 \). In the time domain, the TSMSA for \( C_s(k; t) \) is the sum of two exponentials. For the correlation factor, we obtain

\[ f_{ms}(c, \alpha) = 1 - \frac{2c}{l(1 - c + \alpha) + 2c}. \]

In the limit of small concentration, large dimension and large \( \alpha \), \( f_{ms} = 1 \).

We also developed an approximate kinetic theory that has the structure of a simple mode coupling approximation (SMCA) using the time unordered series. In this approximation, the memory function describes repeated scattering events of a trace particle and a dominant species fluctuation on adjacent lattice sites. Between any pair of scattering events, the trace particle and the density fluctuation of the dominant species each propagate independently in time according to the exact dynamics for a single density fluctuation. This is an approximation however, since such density fluctuations do not propagate independently between scattering events. The mathematical expression that results from summing the irreducible memory function diagrams in this approximation has the same form as appears in mode coupling theories.\(^11\) We derived the following set of equations for the self-correlation function \( C_s \), the memory function \( M_{n,n'} \), and the irreducible memory function \( M_{n,n'}^{irr,mc} \):

\[ \frac{\partial}{\partial t_1} C_s(1t_1; 1't_1) = \sum_{1''} Q_{11}^{(c)}(1; 1'') C_s(1''t_1; 1't_1) + \sum_{1''} \int_{t_1'}^{t_1} dt_1'' M(1t_1; 1''t_1) C_s(1''t_1; 1't_1) \quad (3) \]

\[ M(1t_1; 1't_1) = \sum_{n,n'} M_{n,n'}(1t_1; 1't_1) \quad (4) \]
\[ M_{n,n'}(1t_1; 1't_1') = M_{n,n'}^{\text{irr,mc}}(1t_1; 1't_1') - \frac{1}{\gamma 2(1-c)} \sum_{n''} \sum_{1'} \int_{t_1}^{t} M_{n,n''}^{\text{irr,mc}}(1t_1; 1''t_1')M_{n'',n'}(1''t_1'; 1't_1')dt_1'' \]

\[ M_{n,n'}^{\text{irr,mc}}(R_1S_t; R_1'S_{t'}) = \sum_{R'_1' R_2' R_3'} Q_{12}^{(c,n)}(R_1S_t; R_1'S_{t'}; R_2'S_{t} R_3'S_{t'})C_s(R_2'S_{t} R_3'S_{t'}; R_1'S_{t'})\chi_{11}(R_2'S_{d} R_3'S_{d'}; R_1'S_{t})Q_{21}^{(c,n)}(R_2'S_{t}, R_2'S_{d}; R_1'S_{d}) \]

where \( \chi_{11}(R_{d} R_{d'}; R_{s} R_{s'} d') \) is the response function for the dominant species that has a simple analytic form. To compare the SMCA with the results of computer simulations, we solve Eqn. 3 to 6 in Fourier space,

\[ \frac{d}{dt} C_s(k; t) = Q_{11}(k)C_s(k; t) + \int_{0}^{t} M(k; t-t')C_s(k; t')dt' \]

\[ M(k; t) = \sum_{n,n'} M_{n,n'}(k; t) \]

\[ M_{n,n'}(k; t) = M_{n,n'}^{\text{irr,mc}}(k; t) - \frac{1}{\gamma 2(1-c)} \sum_{n''} \int_{0}^{t} M_{n,n''}^{\text{irr,mc}}(k; t-t')M_{n'',n'}(k; t')dt' \]

\[ M_{n,n'}^{\text{irr,mc}}(k; t) = \gamma^2 c(1-c) \times \frac{1}{L^d} \sum_{k'} \left( e^{-i(k-k') \cdot n} - e^{ik' \cdot n} \right) \left( e^{-i(k-k') \cdot n'} - e^{-ik' \cdot n'} \right) \times C_s(k'; t) \exp \left( -\gamma \alpha 2 \sum_{i=1}^{d} (1 - \cos(k_i - k_i')) t \right) \]

where \( k_i' \) is the \( i \) component of the vector \( k' \). We employ a simple forward time algorithm

\[ C_s(k; t_{i+1}) = C_s(k; t_i + \Delta t) \approx C_s(k; t_i) + (\Delta t) \frac{d}{dt} C_s(k; t_i) \]

to solve for \( C_s(k; t) \) with the initial conditions that \( C_s(k; 0) = 1 \) for all \( k \) and

\[ M_{n,n'}^{\text{irr,mc}} = M_{n,n'}(0; 0) = \gamma^2 2c(1-c) \times \left( \delta(n; n') - \delta(n; -n') e^{ikn'} \right) \times \left( 1 - \delta(n \cdot n', 0) \right) \]

where \( \delta(a; b) \equiv \delta(a_1, b_1) \ldots \delta(a_d, b_d) \) for any two vectors \( a = (a_1, \ldots, a_d) \) and \( b = (b_1, \ldots, b_d) \). We calculate the simple mode coupling prediction for the correlation factor by using \( C_s(k; t) \) for \( |k| = \pi/10 \) in the (1,0) or (1,0,0) direction assuming that \( C_s(k; t) \) is of the form \( \exp(-|k|^2 f(c, \alpha) \gamma (1-c)t) \) at the longest times studied.

### III. Simulation Methods

To simulate the excluded volume lattice gas, we considered a hyper-cubic lattice with periodic boundary conditions in two and three dimensions. For two dimensional simulations, the system was a square with \( L^2 \) sites, and for three dimensions it was a cube with \( L^3 \) lattice sites. To generate an initial state of the system, we placed the appropriate number of particles on different sites such that all configurations are equally likely. Because of the simple interactions between particles in this model, this procedure correctly sampled the canonical distribution; no further equilibration of the system was needed. We outline our \( O(N) \) procedure for generating a state from the canonical ensemble in Appendix A. We chose an initial state with a fixed number of particles to eliminate the statistical error in dynamical properties that result from fluctuations in the number of particles. Such fluctuations would occur if one generates an initial state from the grand canonical ensemble by placing a particle at each site with probability \( c \), the method employed by previous authors.\(^1,3,10\)

After generating an initial state, we used an algorithm for the dynamics that is a generalization of the continuous time algorithm used to simulate the dynamics of spin systems;\(^12,11\) one of us stated this algorithm elsewhere.\(^14\)

We calculated the tracer diffusion coefficient by the expression

\[ D_{tr}(c, \alpha) = \frac{1}{2dt} \left\langle r^2(t) \right\rangle \]

where \( \left\langle r^2(t) \right\rangle \) was the ensemble averaged mean square displacement of a particle in a time interval \( t \). It is a standard procedure in the literature to report the correlation factor \( f(c, \alpha) \) defined previously. To calculate the IISF, we computed the time correlation function for a Fourier mode of a finite lattice system

\[ C_s(k; t) = \left\langle e^{-ik \cdot r(0)} e^{ik \cdot r(t)} \right\rangle \]

where \( r(0) \) and \( r(t) \) were positions of the trace particle.

For the \( \alpha = 1 \) situation in which the trace and dominant particles have the same transition rate, we performed one component simulations with periodic boundary conditions and analyzed the dynamics of each particle as if it were the trace particle. We considered a low \( c = 0.1 \), a medium \( c = 0.5 \), and a high \( c = 0.9 \)
concentration and used \( L = 100 \) and \( L = 20 \) for two and three dimensions respectively. The IISF was calculated for \( |\mathbf{k}| = (\pi/10)\sqrt{d}, (6\pi/10)\sqrt{d}, \pi\sqrt{d} \) along the \((1,1)\) or \((1,1,1)\) direction and \( |\mathbf{k}| = \pi/10, \pi/5 \) along the \((1,0)\) or \((1,0,0)\) direction. We performed 50 runs at the two lower concentrations and 30 runs at the highest concentration. In time units of \( \gamma^{-1} \), the \( d = 2 \) simulations were 150, 300, and 1500 time units long for \( c = 0.1 \), \( c = 0.5 \), and \( c = 0.9 \) respectively. For \( d = 3 \), the simulations were 150, 250, and 1200 time units long for \( c = 0.1 \), \( c = 0.5 \), and \( c = 0.9 \) respectively.

The strictest test for the analytic theories is at high concentration, so we focused our attention on \( c = 0.9 \) in both two and three dimensions for systems in which \( \alpha = 0.1, 0.5, 2, 10 \). All previous simulations on systems in which \( \alpha \neq 1 \) used multiple trace particles to obtain better statistics.\(^\text{"1, 15} Our preliminary calculations showed that dynamic properties such as the mean square displacement of a trace particle were sensitive to the number of trace particles in the system. We instead chose to run simulations with only a single trace particle at smaller system sizes, which allowed us to perform many more runs. For each \( \alpha \neq 1 \) system, we performed 2000 runs. Each run lasted 1500 and 1200 time units in \( d = 2 \) and \( d = 3 \) respectively.

To determine the optimal system size for the \( \alpha \neq 1 \) systems, we simulated one component systems with \( c = 0.90 \) for a number of different system sizes and calculated the tracer diffusion coefficient \( D(c, V) \). We assumed that \( D(c, V) \) was linear in \( V^{-1} \) for our system sizes and used a best fit line to determine \( D_{\infty}(c) \) in the limit of infinite system size. We then estimated the systematic error due to finite system size by \( |D(c, V) - D_{\infty}(c)| \). There is also systematic error associated with the introduction of a single trace particle which we estimated by the difference in the diffusion coefficient between two systems with \( N \) and \( N+1 \) particles. A straightforward calculation shows that this error is given by \( f(c)V^{-1} \). We chose a system size such that both of these systematic errors were less than one percent of \( D(c, V) \). This resulted in using \( L = 30 \) and \( L = 10 \) in two and three dimensions respectively for the \( \alpha \neq 1 \) systems.

\section*{IV. COMPARISON WITH THEORY}

\subsection*{A. Correlation Factor}

Tables I and II present results for the correlation factor for \( \alpha = 1 \) and \( \alpha \neq 1 \) respectively. For all systems, the two site multiple scattering and simple mode coupling approximations overestimate the value of the correlation factor, and the deviation is larger for the TSMSA than the SMCA. The predictions of the kinetic theories are more accurate for small concentrations, higher dimensions and larger values of \( \alpha \). For one component systems, we calculate the correlation factor from simulation data using both the mean square displacement of the particle as well as the rate of decay of \( C_s(k; t) \) for \( |\mathbf{k}| = \pi/10 \) in the \((1,0)\) and \((1,0,0)\) direction. The similarity of these results suggests that calculating the SMCA prediction for the correlation factor from \( C_s(k; t) \) at this small wave vector is an accurate estimate. Unfortunately, it is not possible to perform this calculation for all systems due to memory constraints.

\begin{table}
\centering
\caption{The correlation factors for \( \alpha = 1 \). \( f_{\alpha}(c) \) is the correlation factor calculated from simulation using the mean square displacement of the trace particle. \( f_k(c) \) is the correlation factor obtained from the simulation results for the IISF for \( |\mathbf{k}| = \pi/10 \) in the \((1,0)\) or \((1,0,0)\) direction assuming that the magnitude of this wave vector is small enough so that the decay rate of the IISF is related to the tracer diffusion coefficient. The statistical error is less than 0.2% in both of these estimates. \( f_{\alpha}(c) \) is the two site multiple scattering approximation prediction given in Eqn. 2. \( f_{\alpha}(c) \) is an estimate of the correlation factor for the simple mode coupling approximation using the decay rate of the numerical prediction for the IISF for \( |\mathbf{k}| = \pi/10 \) in the \((1,0)\) or \((1,0,0)\) direction.}
\begin{tabular}{|c|c|c|c|c|}
\hline
\( d \) & \( c \) & \( f_{\alpha}(c) \) & \( f_k(c) \) & \( f_{\alpha}(c) \) \\
\hline
2 & 0.10 & 0.943 & 0.955 & 0.966 & 0.956 \\
2 & 0.50 & 0.715 & 0.710 & 0.818 & 0.790 \\
2 & 0.90 & 0.511 & 0.505 & 0.647 & 0.598 \\
3 & 0.10 & 0.974 & 0.965 & 0.979 & 0.971 \\
3 & 0.50 & 0.845 & 0.838 & 0.882 & 0.866 \\
3 & 0.90 & 0.694 & 0.688 & 0.753 & * \\
\hline
\end{tabular}
\end{table}

\begin{table}
\centering
\caption{The correlation factors for \( \alpha \neq 1 \) and \( c = 0.90 \). \( f_{\alpha}(c) \) is the correlation factor from the mean square displacement of the trace particle in the simulation results. The statistical error is about 1% in each of these estimates. \( f_{\alpha}(c) \) is the correlation factor from the two site multiple scattering approximation using Eqn. 2.}
\begin{tabular}{|c|c|c|}
\hline
\( d \) & \( \alpha \) & \( f_{\alpha}(c) \) \\
\hline
2 & 0.1 & 0.108 & 0.250 \\
2 & 0.5 & 0.348 & 0.500 \\
2 & 1.0 & 0.511 & 0.647 \\
2 & 2.0 & 0.667 & 0.778 \\
2 & 10.0 & 0.917 & 0.944 \\
3 & 0.1 & 0.218 & 0.357 \\
3 & 0.5 & 0.530 & 0.625 \\
3 & 1.0 & 0.694 & 0.753 \\
3 & 2.0 & 0.807 & 0.854 \\
3 & 10.0 & 0.947 & 0.966 \\
\hline
\end{tabular}
\end{table}
FIG. 1: A comparison of theory and simulation for the normalized incoherent intermediate scattering function $C_s(k; t)$ as a function of time for $|k| = (\pi/10)\sqrt{2}$ along the (1, 1) direction with $d = 2$, $c = 0.10$ and $\alpha = 1$. The circles are the simulation results, the dash dot line is the mean field approximation, and the solid line is the simple mode coupling approximation. The simple mode coupling and two site multiple scattering approximations are indistinguishable from each other. Time is in units of $\gamma^{-1}$.

B. Time Correlation Function

Fig. 1 compares simulation results for the IISF of a $d = 2$ system for low concentration, $c = 0.1$, and small wave vector with the predictions of the three approximate theories. The mean field approximation is fairly accurate, but both the TSMSA and the SMCA are more accurate (and indistinguishable from one another in the figure). At large wave vectors (not shown in the figure), the TSMSA still accurately corrects the MFA, but the SMCA does not. The SMCA correction to the MFA is small, but it is in the wrong direction at short times, decaying more quickly than the MFA, whereas the simulation data decays less quickly than the MFA. Although the SMCA prediction for the IISF is only slightly less than the MFA at these short times, it is the only time we find that either the TSMSA or the SMCA decays more quickly than the MFA.

Fig. 2a and 2b show two dimensional results for an intermediate concentration, $c = 0.50$, at a small and large wave vector respectively. For all wave vectors, the MFA predicts a decay that is too rapid and does not accurately predict the simulation results. For the small wave vector, the TSMSA is more accurate than the MFA, and the SMCA is slightly more accurate than the TSMSA. The use of the full response function for the dynamics between scattering events provides the most accurate approximation for the dynamics on long length scales. For the large wave vector, the TSMSA is more accurate than the SMCA. An approximation that describes two site dynamics exactly very accurately predicts the dynamics on the shortest length scales of the lattice system. Fig. 3 displays results at the same concentration for a small wave vector in three dimensions. All three approximate kinetic theories predict the simulation data more accurately in three dimensions than in two.

Fig. 4a and 4b show results for $c = 0.90$ and a large wave vector in two and three dimensions respectively. The MFA is even less accurate at this high concentration than at the intermediate concentration. The TSMSA is more accurate than the MFA, but the SMCA is the most accurate theory. The three kinetic theories have this qualitative trend in predicting the simulation data at all wave vectors for this high concentration. Comparing Fig. 4a and Fig. 4b shows the improved accuracy of the three approximate kinetic theories in three dimensions. We see this improvement for all $k$, $c$ and $\alpha$.

To our knowledge, the only other work that compared
the TSMSA and the SMCA. Time is in units of $\gamma^{-1}$. It is difficult to distinguish between the two theories at small wave vectors but not as good at large wave vectors. Since the FSTKE theory gave an accurate expression for the correlation factor $f(c, 1)$, it was not surprising that they accurately predict the long wavelength behavior of the IISF. From our comparison of simulation with the two site multiple scattering approximation and simple mode coupling approximation at small wave vectors, it is clear that neither approximation describes the IISF at small wave vectors as well as the FSTKE theory. For large wave vectors, we compare the results of our two theories for $d = 2$ with $c = 0.701$ and $|k| = \pi \sqrt{2}$ along the $(1, 1)$ direction for $d = 3$. The other parameters are $c = 0.90$ and $\alpha = 1$. The circles are the simulation results, the dash dot line is the mean field approximation, the dashed line is the two site multiple scattering approximation, and the solid line is the simple mode coupling approximation. It is difficult to distinguish between the TSMSA and the SMCA. Time is in units of $\gamma^{-1}$.

Fig. 5 shows the results for $d = 2$ and $c = 0.9$ at a small wave vector for a range of $\alpha$. The simulation results for $C_s$ converge towards the mean field prediction as $\alpha$ increases. We observe this trend for the simulation results for all the wave vectors at the high concentration. Conversely, the IISF most significantly deviates from the mean field prediction at small values of $\alpha$. Fig. 6a and 6b present a comparison of all three approximate kinetic theories with simulation results for $\alpha = 0.1$ in two and three dimensions respectively. The MFA predicts the fastest decay, the TSMSA gives the next fastest decay while the SMCA decays the slowest of the three and most accurately predicts the simulation results. We observe these qualitative trends at all wave vectors. These results point out the need for more accurate kinetic theo-

![Fig. 3: A comparison of theory and simulation for the normalized incoherent intermediate scattering function $C_s(k;t)$ for $d = 3$, $c = 0.50$ and $\alpha = 1$. The wave vector is $|k| = (\pi/10)\sqrt{3}$ along the $(1, 1, 1)$ direction. The circles are the simulation results, the dash dot line is the mean field approximation, the dashed line is the two site multiple scattering approximation, and the solid line is the simple mode coupling approximation.](image)

![Fig. 4: A comparison of theory and simulation for the normalized incoherent intermediate scattering function $C_s(k;t)$ as a function of time for $|k| = (\pi/5)\sqrt{2}$ along the $(1, 1)$ direction for $d = 2$ (a) and $|k| = (\pi/5)\sqrt{3}$ along the $(1, 1, 1)$ direction for $d = 3$ (b). The other parameters are $c = 0.90$ and $\alpha = 1$. The circles are the simulation results, the dash dot line is the mean field approximation, the dashed line is the two site multiple scattering approximation, and the solid line is the simple mode coupling approximation.](image)
FIG. 5: The results of computer simulations for $d = 2$, $c = 0.90$ and $|k| = (\pi/5)\sqrt{2}$ along the $(1,1)$ direction for a wide range of values for $\alpha$. The dash dot line is the mean field approximation, which is independent of $\alpha$. The simulation results are for $\alpha = 0.1$ (squares), $\alpha = 0.5$ (circles), $\alpha = 1$ (upward pointing triangle), $\alpha = 2$ (downward pointing triangle), and $\alpha = 10$ (diamond). The simulation results approach the mean field prediction as $\alpha$ gets larger.

We also note that for $\alpha = 10$, $d = 2$ and small wave vectors, the SMCA decays more slowly than the simulation results. This is the only system in which any of our approximate kinetic theories show this anomalous behavior.

V. DISCUSSION AND CONCLUSION

We have compared simulation results for the incoherent intermediate scattering function with the three kinetic theories we developed in the previous paper. In general, the three theories were more accurate for lower concentrations, higher dimensions and large values of $\alpha$. The mean field approximation was very accurate for small concentrations and large values of $\alpha$. More generally, this approximation predicted a decay for the IISF that was too rapid compared with the simulation results. For all systems, the two site multiple scattering approximation was more accurate than the MFA but its results decayed more quickly than the simulation results. This approximation was very accurate for large wave vectors at low and intermediate concentrations and had the advantage of a simple analytic form. In most cases, the simple mode coupling approximation gave a correction to the TSMSA that decayed more quickly than the simulation results. This approximation provided the largest correction for large concentrations and small values of $\alpha$. Also, both the TSMSA and the SMCA predicted correlation factors that were too large, which explained the prediction of an IISF that decayed too quickly compared with simulation results at small wave vectors.

The comparison of the TSMSA and the SMCA with simulation results allows us to evaluate the merits of using the time ordered and time unordered series for the time correlation function, developed in the previous paper, to construct approximate kinetic theories. Any approximation that consists of summing a subset of time ordered diagrams for the irreducible memory function is completely consistent with the excluded volume effect in that each intermediate state in each diagram has all the excitations on different sites. The TSMSA has this characteristic. Consistency with the excluded volume effect is probably related to the accuracy of the TSMSA for large wave vectors, since consistency with the excluded volume effect is very important for a proper description on the shortest length scales. Summing a larger set of time ordered diagrams for the irreducible memory function than in the TSMSA could produce a more accurate result for simulation results.
higher concentrations, especially for large wave vectors. In the time unordered series, there are individual diagrams that violate the excluded volume effect, although the overall series is still formally exact. From this series, it is possible to obtain mode coupling approximations in which each of two excitations in the irreducible memory propagates independently according to the exact correlation function for single excitations. Our SMCA led to accurate results for small wave vectors and high concentrations. We anticipate that the time unordered series will be useful in developing new approximations that will more accurately describe the IISF for small wave vector, high concentration and small $\alpha$.

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APPENDIX A: EQUILIBRIUM DISTRIBUTION

We generate a state of the system from the equilibrium distribution of the canonical ensemble through the following algorithm. Firstly, develop a one to one correspondence between the integers 1...$M$ and each site on the lattice. Create an array with $M$ entries, and let the $i$ element of the array be the integer $i$. To determine the position of the first particle, pick a random number from $j_1 \in \{1...M\}$ and put the particle at the site that corresponds to $j_1$ entry in the array. Set the $j_1$ element of the array be the $M$ element of the array. To find the position of the $p$ particle, pick a random number $j_p \in \{1...M-p+1\}$ where $M-p+1$ is the number of empty sites and put the $p$ particle at the site designated by the $j_p$ element of the array. Set the $j_p$ element of the array be the $M-p+1$ element of the array. Iterate this procedure the necessary number of times. Note that if there are $n$ empty lattice sites, then the first $n$ elements in the array correspond to these empty sites. Replacing the element of the array that has just been selected with an integer that corresponds to an empty sites guarantees that the integers that correspond to the empty sites are at the beginning of the array. This is an $O(N)$ process.