Kinetic theories of dynamics and persistent caging in a one-dimensional lattice gas

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The one-dimensional, single-occupancy lattice gas exhibits highly cooperative particle motion and provides an interesting challenge for theoretical methods designed to describe caging in liquids. We employ this model in an effort to gain insight into caging phenomena in more realistic models of liquids, using a diagrammatic kinetic theory of density fluctuations to develop a series of approximations to the kinetic equations for the van Hove self-correlation function. The approximations are formulated in terms of the irreducible memory function, and we assess their efficacy by comparing their solutions with computer simulation results and the well-known subdiffusive behavior of a tagged particle at long times. The first approximation, a mode coupling theory, factorizes the 4-point propagators that contribute to the irreducible memory function into products of independent single-particle propagators. This approximation fails to capture the subdiffusive behavior of a tagged particle at long times. Analysis of the mode coupling approximation in terms of the diagrammatic kinetic theory leads to the development of two additional approximations that can be viewed as diagrammatic extensions or modifications of mode coupling theory. The first, denoted MC1, captures the long-time subdiffusive behavior of a tagged particle. The second, denoted MC2, captures the subdiffusive behavior of a tagged particle and also yields the correct amplitude of its mean square displacement at long times. Numerical and asymptotic solutions of the approximate kinetic equations share many qualitative and quantitative features with simulation results at all timescales.

liquids | mode coupling

Dense liquids exhibit highly correlated motions of constituent particles. Understanding the dynamics of particle motion can give deep insight into both microscopic and macroscopic properties of liquids, including the diffusive properties of labeled particles and macroscopic transport coefficients (1). In many dense liquids, correlated particle motion is closely related to the phenomenon of caging, in which the motion of each particle is severely constrained by the presence of other nearby particles. Each particle is said to be surrounded by a "cage" of neighboring particles, and in order for a particle to move an appreciable distance, a collective rearrangement of its caging particles must occur.

Characterizing the breakdown of a cage is of paramount importance in understanding the properties of many liquids, including atomic, polymeric, and colloidal fluids. For example, caging is thought to dominate the dynamics of liquids near the glass transition, and it plays an important role in polymer physics, where entanglement effects at the microscopic level affect macroscopic properties such as viscosity and elasticity.

This article examines the development of approximate kinetic theories for a one-dimensional, single-occupancy lattice gas in which particles undergo symmetric, continuous-time random walks subject to the constraint that they cannot pass through each other. Once particles occupy the lattice, they cannot change their relative ordering, and the motion of each particle is always constrained by the same two neighboring particles. This is an extreme form of caging, with each particle "persistently caged" by the presence of its neighboring particles. Large excursions by any particle require highly cooperative motion of many other particles.

The one-dimensional lattice gas has attracted much attention since its first computer simulation study (2), with early work on the model establishing that the long-time mean square displacement of a tagged particle grows as the square root of time (2–8). In a significant achievement, Arratia (5) rigorously proved that the asymptotic behavior of the mean square displacement (MSD) of a tagged particle is

$$\mathrm{MSD}(t) \sim 2\left(\frac{1-c}{c}\right)\sqrt{\frac{\gamma t}{\pi}} \quad \text{as } t \to \infty, \qquad [1]$$

where c is the concentration of particles, each of which has the same characteristic jump rate γ. This growth is slower than the linear dependence expected for diffusive motion, which is characteristic of particle motion in higher-dimensional lattice gas models. As a consequence, it is said that a tagged particle in the one-dimensional lattice gas undergoes anomalous, subdiffusive motion.

Our approach to the one-dimensional lattice gas uses a diagrammatic kinetic theory of fluctuations in equilibrium fluids (9–13) to systematically develop approximate kinetic theories. One such approximation of interest is the mode coupling theory of Götze and coworkers (14, 15), which is widely considered a theory of caging. [For an extensive review of mode coupling theory, see Das (16).] The diagrammatic theory facilitates the construction of a mode coupling theory, as well as other related theories.

By comparing theoretical predictions of the various approximations with computer simulation data and the exactly characterized long-time MSD of a trace particle, the effectiveness of the theories can be evaluated. Most importantly, theoretical insights gained in the study of the one-dimensional lattice gas suggest ways to develop theories of caging in more complicated and realistic models of liquids.

This article focuses on the problem of stochastic dynamics in a one-dimensional lattice gas. Previous studies have also investigated related models governed by stochastic dynamics, including one-dimensional systems with continuous coordinates (17–21), quasi-one-dimensional fluids in narrow pores (22–24), and single-occupancy lattice gases in higher dimensions (12, 13, 25–28). Additionally, this work focuses on two-point correlation functions that describe the dynamics of the system of interest. Other recent extensions of mode coupling theory have been concerned with more complicated multipoint functions and with dynamic heterogeneity (29–31).

Model System and Diagrammatic Theory

Consider two types of particles, called the trace and dominant species, that occupy sites of a large but finite one-dimensional lattice with unit spacing and periodic boundary conditions. Each particle occupies a single lattice site and no two particles may occupy

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the same site at the same time. The trace species is present on the lattice with concentration c_t, and the dominant species is present with concentration c_d. We focus on the trace-dominant limit in which $c_t \ll c_d$, with the total concentration of particles denoted by $c \approx c_d$. For the grand canonical ensemble, every allowed state has an energy of zero, and the particle density fluctuations at distinct sites are statistically independent.

The dynamics of the system are stochastic, with each particle having a nonzero, species-dependent transition rate only to empty nearest neighbor lattice sites. A trace particle makes transitions to each unoccupied nearest neighbor lattice site with rate γ_t, and a dominant particle makes transitions to each unoccupied nearest neighbor lattice site with rate γ_d. The complete state of the system is given by listing the location and type of each particle on the lattice, and the time evolution of the probability distribution of states, conditional on an initial distribution, is governed by a master equation. This Markovian dynamics satisfies a detailed balance condition with respect to the equilibrium probability distribution.

Time Correlation Functions and Kinetic Equations. The fundamental correlation function that describes the motion of a tagged particle is the trace correlation function $C_t(R,t)$, which is the probability that a trace particle at time t is displaced a distance R from its position at time 0 (12). The Fourier transform of the trace correlation function is

$$\hat{C}_t(k,t) = \sum_R e^{-ikR} C_t(R,t)$$

The sum extends over all lattice sites R, and k takes on values consistent with periodic boundary conditions. [For large systems, the inverse transform can be expressed as $C_t(R,t) = (2\pi)^{-1} \int_{-\pi}^{\pi} dk\, e^{+ikR} \hat{C}_t(k,t)$.] The mean square displacement of a tagged particle is the second spatial moment of $C_t(R,t)$ and can be expressed as $\mathrm{MSD}(t) = -\partial^2 \hat{C}_t(k,t)/\partial k^2|_{k=0}$.

The kinetic equation for the trace correlation function is

$$\partial \hat{C}_t(k,t)/\partial t = Q_{11}(k)\hat{C}_t(k,t) + \int_0^t dt' M(k,t-t')\hat{C}_t(k,t'), \quad [2]$$

where $Q_{11}(k) = -2(1-c)\gamma_t(1-\cos k)$ is the mean field term and $M(k,t)$ is the memory function of the trace particle (12, 13). The memory function can be related to an irreducible memory function M^{irr} by the integral equation

$$M(k,t) = M^{\mathrm{irr}}(k,t) - (2(1-c)\gamma_t(1-\cos k))^{-1} \int_0^t dt' M^{\mathrm{irr}}(k,t-t')M(k,t') \quad [3]$$

It follows from the diagrammatic kinetic theory (12) that for this one-dimensional model the irreducible memory function can be expressed in terms of a scaled irreducible memory function G^{irr} (32),

$$M^{\mathrm{irr}}(k,t) = 8c(1-c)\gamma_t^2(1-\cos k)G^{\mathrm{irr}}(k,t), \quad [4]$$

and the latter can be expressed in terms of a small number of 4-point propagators,

$$G^{\mathrm{irr}}(k,t) = \frac{1}{4}\sum_R e^{-ikR} \times (\chi^{\mathrm{irr}}(R,R+1;0,1;t) + \chi^{\mathrm{irr}}(R,R-1;0,-1;t) - e^{+ik}\chi^{\mathrm{irr}}(R,R-1;0,1;t) - e^{-ik}\chi^{\mathrm{irr}}(R,R+1;0,-1;t)) \quad [5]$$

Note that χ^{irr} is a function of 4 position arguments and a single time argument; we refer to it as the irreducible 4-point propagator. The first and second position arguments (R and $R \pm 1$) correspond to the final positions of a trace particle and dominant particle density fluctuation, respectively, and the third and fourth position arguments correspond to the initial positions of a trace particle and dominant fluctuation, respectively. It is a time-dependent response function for two particle fluctuations that start in the specified initial positions and end at the specified final positions.

The equations for C_t, M, and G^{irr} provide the basis for our theoretical developments and are collectively called the kinetic equations. The diagrammatic theory of Feng and Andersen provides formally exact diagrammatic expressions for C_t and M, and allows the derivation of formally exact diagrammatic expressions for χ^{irr}, which will not be presented in detail here (12, 32). There are two versions of the theory, the time ordered version and the time unordered version. We use the time-ordered version of diagrams.

Another correlation function important to our theoretical development is the dominant correlation function $C_d(R,t)$, which is the normalized time- and position-dependent correlation function of dominant density fluctuations. It can also be expressed as a formally exact diagrammatic series, the form of which is simple and straightforward to sum. The exact solution is $\hat{C}_d(k,t) = \exp(-2\gamma_d(1-\cos k)t)$. It is surprising that this function is the same as the Fourier transform of the probability distribution of a single dominant particle executing a nearest neighbor random walk on an otherwise unoccupied lattice. The close relationship between diagrams for the dynamics of dominant particle density fluctuations and random walk problems is exploited in results presented below.

Kinetic Theories

Mean Field Theory. The simplest nontrivial approximation to the kinetic equations, a mean field theory, sets the memory function equal to zero for all times, yielding the following equation for the trace correlation function:

$$\partial \hat{C}_t(k,t)/\partial t = Q_{11}(k)\hat{C}_t(k,t)$$

The solution of this equation is a simple exponential,

$$\hat{C}_t(k,t) = \exp(-2(1-c)\gamma_t(1-\cos k)t)$$

For this approximation, $\mathrm{MSD}(t) = 2(1-c)\gamma_t t$, and the motion is predicted to be diffusive at all times.

Mode Coupling Theory. In an attempt to incorporate a description of cooperative effects into a theory of the lattice gas, we formulate a mode coupling theory in terms of the irreducible 4-point propagators that contribute to the scaled irreducible memory function. We make the approximation that each irreducible 4-point propagator factorizes into a product of a trace and dominant correlation function,

$$\chi^{\mathrm{irr}}_{\mathrm{MC}}(R,R_d;0,R'_d;t) = C_t(R,t)C_d(R_d-R'_d,t) \quad [6]$$

Although there are a variety of theoretical ideas and approaches that might be called mode coupling theory, Eq. **6** is precisely analogous to the approximations made by using the "simplified mode coupling theory" approach of Götze and coworkers (14, 15). (See also ref. 33.) Because Götze's formulation of simplified mode coupling theory is currently the most familiar and influential formulation of mode coupling theory for dense and supercooled liquids, we refer to this approximation simply as "mode coupling theory." Feng and Andersen motivated an analogous factorization approximation by using the time-unordered diagrammatic theory (12, 13).

Physically, the factorization approximation for the irreducible 4-point propagator implies that the trace particle and dominant

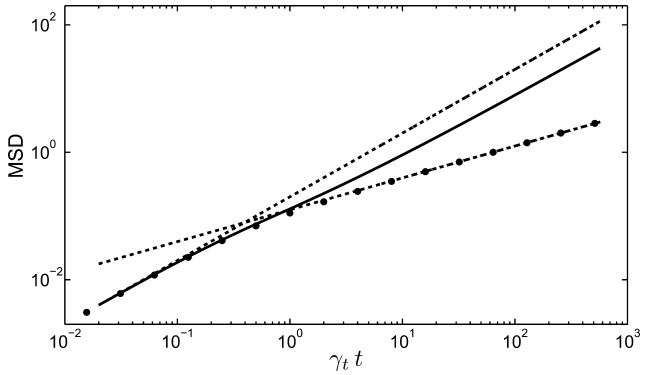

Fig. 1. Test of the mode coupling theory prediction for the MSD of a trace particle for $c = 0.9$ and $\gamma_t = \gamma_d$. The solid line is the mode coupling approximation, points correspond to simulation results, and the straight dashed lines are the mean field approximation (with slope 1) and the exact asymptotic behavior given by Eq. **1** (with slope 1/2).

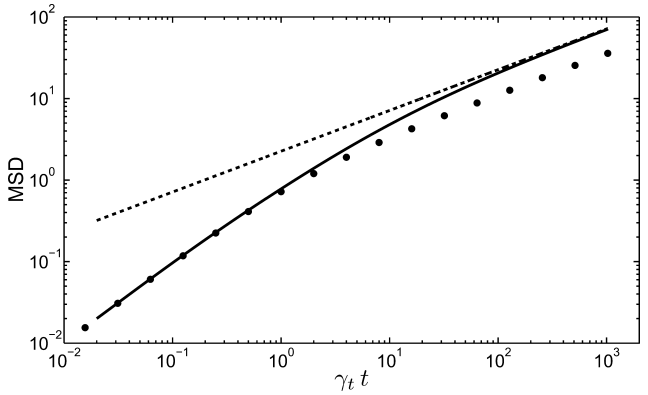

Fig. 2. MSD of the trace particle under approximation MC1 as a function of time, with $c = 0.5$ and $\gamma_t = \gamma_d$. The solid line corresponds to the numerical solution, the dashed line corresponds to the asymptotic solution, and points correspond to simulation results.

fluctuation evolve independently in time according to their respective correlation functions. This approximation gives rise to the following scaled irreducible memory function:

$$G^{\rm irr}_{\rm MC}(k,t) = \frac{1}{2}\int_{-\pi}^{\pi}\frac{dk'}{2\pi}(1-\cos(k-2k'))\hat{C}_t(k-k',t)\hat{C}_d(k',t)$$

The dominant correlation function is known exactly, whereas the trace correlation function is the unknown function of interest. Taken with the other kinetic equations (Eqs. **2**, **3**, and **4**), this expression yields a set of equations that can be solved self-consistently for the trace correlation function. A numerical solution method is described in *Appendix*, and an example of a typical mode coupling approximation result for the MSD of a trace particle is given in Fig. 1. Note that the mode coupling approximation grows more slowly than the mean field approximation, but provides an accurate prediction of the trace particle MSD only for times shorter than γ_t^{-1}. By a time of $2\gamma_t^{-1}$, the simulation results have nearly joined the asymptotic solution given by Eq. **1**, but the mode coupling approximation continues to grow at a much faster rate, reaching a value that is an order of magnitude larger than the simulation result at the longest times in the figure. The numerical results strongly suggest that mode coupling theory, like the mean field theory, predicts diffusive behavior at long times.

Modified Mode Coupling Approximation 1. To improve on the mode coupling approximation just formulated, we focus on properties of the function $\chi^{\rm irr}(t)$, which describes the joint propagation of a trace particle and a dominant particle density fluctuation for a time t. In higher dimensions, graphical versions of mode coupling theory neglect diagrams in which the two fluctuations interact (and hence do not propagate independently) (12, 34, 35). Diagrams that contain such interactions are connected, in the sense that it is possible to construct a path from any point on the graph to any other point on the graph that proceeds along bonds and vertices in the graph. Thus, one way to construct a theory that contains the physical ideas of mode coupling theory for the present problem is to neglect all connected diagrams in $\chi^{\rm irr}$. The results obtained depend on which graphical series for $\chi^{\rm irr}$ is used. For the current problem, using the time-ordered series of Feng and Andersen (12) yields a useful approximation.

When a diagrammatic theory is constructed that retains only the disconnected diagrams in the time-ordered series for $\chi^{\rm irr}$, the last two $\chi^{\rm irr}$ terms in Eq. **5** are zero, since only connected diagrams contribute to their value. This is a special feature of the one-dimensional model and the time-ordered version of the diagrammatic theory. (In higher dimensions, and for the time-unordered version of the theory, there are disconnected diagrams that allow two density fluctuations to exchange relative position.) The mode coupling factorization approximation can be used to approximate the remaining two terms in $G^{\rm irr}$. This gives a modified mode coupling approximation,

$$G^{\rm irr}_{\rm MC1}(k,t) = \frac{1}{2}\int_{-\pi}^{\pi}\frac{dk'}{2\pi}\hat{C}_t(k-k',t)\hat{C}_d(k',t)$$

This approximation for $G^{\rm irr}$, together with Eqs. **2**, **3**, and **4**, defines a modified mode coupling theory for the trace correlation function, which we denote MC1.

By using the asymptotic method discussed in *Appendix*, a long-time solution of the MC1 equations leads to the result that the mean square displacement of the trace particle grows subdiffusively,

$$\mathrm{MSD}_{\rm MC1}(t) = 4\left(\frac{1-c}{c}\right)\sqrt{\frac{\gamma_d t}{\pi}}$$

for $\gamma_t > 0$. This result differs from the exact asymptotic result in Eq. **1**, which is applicable to the case in which $\gamma_t = \gamma_d$, by a factor of 2. Nevertheless, the modified mode coupling approximation MC1 captures an essential qualitative feature of the exact dynamics that the mode coupling theory does not.

Results for the MSD of a trace particle are shown in Fig. 2, and numerical results for the trace correlation function are compared with simulation results for various choices of wavevector in Fig. 3. The MC1 approximation for $G^{\rm irr}$ is exact at initial time because at

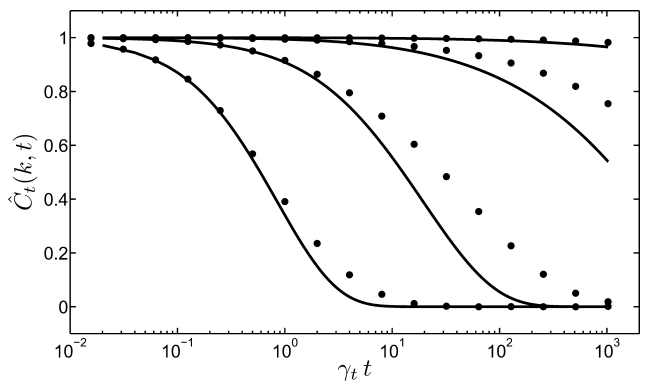

Fig. 3. Trace correlation function under approximation MC1 as a function of time for various choices of wavevector, with $c = 0.5$ and $\gamma_t = \gamma_d$. Results include numerical solutions (solid lines) and simulation data (points) for wavevectors $(2\pi/200)$, $4(2\pi/200)$, $16(2\pi/200)$, and $64(2\pi/200)$. The correlation function at smaller wavevectors decays more slowly.

$t = 0$, both the neglect of connected diagrams and the factorization of the disconnected diagrams are exact. As a result, the short-time behavior of the correlation functions predicted by the MC1 approximation is correct for all wavevectors. However, the figure shows that at longer times the predicted correlation functions decay more rapidly than the simulation results.

This approximation provides a vast improvement over the mode coupling theory in describing the dynamics of a trace particle. The last two χ^{irr} terms in Eq. **5** are associated with trace and dominant fluctuations that exchange relative position, and at long times, the contribution by these terms is overestimated by the factorization approximation. This overestimation is apparently related to the fact that Eq. **6** is exact for a one-dimensional model in which there is no single-occupancy restriction and more than one particle can occupy the same lattice site at the same time with no energy penalty. Such a model allows a trace particle and a dominant particle to exchange their relative positions with no difficulty and clearly allows the trace particle to diffuse at long times. Making the factorization approximation in Eq. **6** for all values of the position arguments neglects the essential physical feature that leads to caging in the single-occupancy lattice gas, and the resulting mode coupling theory fails to predict subdiffusive behavior for a trace particle at long times. The MC1 approximation makes the factorization approximation only for the first two terms in Eq. **5**, in which the relative positions of the trace particle and dominant fluctuation are the same in the initial and final configurations. It approximates the last two terms as zero because they contain only connected diagrams, and as a result, it describes caging in the single-occupancy model in a qualitatively correct way.

Modified Mode Coupling Approximation 2. In this section, we modify the previous approximation by considering properties of the disconnected diagrams that appear in the expression for G^{irr}. Although the approximation in which only disconnected diagrams are kept is exact at $t = 0$, there are several indications that the previous approximation underestimates the value of the first two terms in G^{irr} as time progresses.

The strongest of these indications comes from the evaluation of χ^{irr} for the situation in which the trace particle is immobile ($\gamma_t = 0$) and the dominant fluctuation jumps with its usual transition rate. In this case, both C_t and χ^{irr} can be evaluated exactly because the diagrams that appear are particularly simple. When the trace particle is immobile, $C_t(R,t) = \delta_{R,0}$ for all t, and it can be shown that $\chi^{\text{irr}}(R,R';0,+1;t)$ is zero for $R \neq 0$ and for $R' \leq 0$. Additionally, for $R' > 0$, the 4-point propagator is exactly equal to the time-dependent probability distribution of a single dominant particle executing a random walk on the positive integers, given that it started at position 1. For sufficiently long times and $R' > 0$, this probability distribution is approximately double that of a particle executing a random walk on all integers, given that it started at position $+1$. This implies that for long times, for the case in which $\gamma_t = 0$, $\chi^{\text{irr}}(R,R'+1;0,+1;t) \approx 2C_t(R,t)C_d(R',t)$ for $R' \geq R$. This approximation does well at long times at the expense of overestimating the zero time value of the propagator.

Considering the special case of χ^{irr} with an immobile trace particle is physically relevant because the dominant fluctuation behaves diffusively and the trace particle is expected to behave subdiffusively. For sufficiently long times, the size of a typical excursion taken by the trace particle is dwarfed by the size of a typical excursion taken by the dominant fluctuation, and from the perspective of the dominant fluctuation, the trace particle appears immobile.

Using the previous analysis as motivation, we now include a factor of 2 with the factorization approximation to construct a second modified mode coupling theory, denoted MC2:

$$\begin{aligned}\chi^{\text{irr}}_{\text{MC2}}(R,R+1;0,+1;t) &= \chi^{\text{irr}}_{\text{MC2}}(R,R-1;0,-1;t)\\ &= 2C_t(R,t)C_d(R,t)\end{aligned}$$

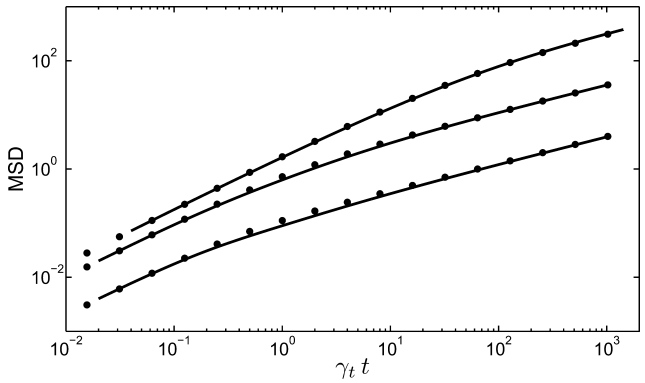

Fig. 4. MSD of the trace particle under approximation MC2 as a function of time, with $\gamma_t = \gamma_d$ and various choices of c. Solid lines correspond to the numerical solutions and points correspond to simulation results. From top to bottom, the concentration of particles is $c = 0.1$, 0.5, and 0.9.

Fedders first introduced a similar factorization with a factor of 2 in an early theoretical treatment of the one-dimensional lattice gas (3). This approximation gives the following expression for G^{irr},

$$G^{\text{irr}}_{\text{MC2}}(k,t) = \int_{-\pi}^{\pi} \frac{dk'}{2\pi} \hat{C}_t(k-k',t)\hat{C}_d(k',t)$$

With the kinetic equations for C_t, M, and M^{irr}, this can be solved self-consistently for C_t by numerical and asymptotic methods. It can be shown that the mean square displacement of the trace particle grows subdiffusively at long times,

$$\text{MSD}_{\text{MC2}}(t) = 2\left(\frac{1-c}{c}\right)\sqrt{\frac{\gamma_d t}{\pi}}$$

for $\gamma_t > 0$. When $\gamma_t = \gamma_d$, this is equivalent to the exact asymptotic result given in Eq. **1**. Results for the MSD of a trace particle are shown in Fig. 4, and numerical results for the trace correlation function are compared with simulation results for various choices of wavevector in Fig. 5. It can be seen that the MSD is slightly underestimated at intermediate times, and that the approximation does best at low concentrations. Qualitatively similar results are found for the trace correlation function at lower and at higher density, and the MC2 approximation, when compared with the MC1 approximation, leads to improved long-time agreement with simulation data at all concentrations. Fig. 6 compares the MSD results from the MC1 and MC2 approximations for the case in which the

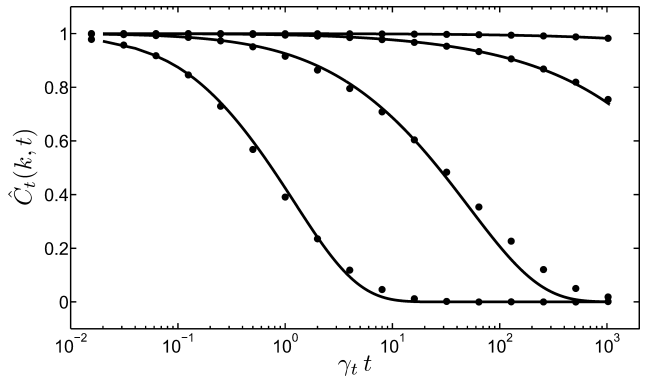

Fig. 5. Trace correlation function as a function of time under approximation MC2 for various choices of wavevector, with $c = 0.5$ and $\gamma_t = \gamma_d$. Results include numerical solutions (solid lines) and simulation data (points) for wavevectors $(2\pi/200)$, $4(2\pi/200)$, $16(2\pi/200)$, and $64(2\pi/200)$. The correlation function at smaller wavevectors decays more slowly.

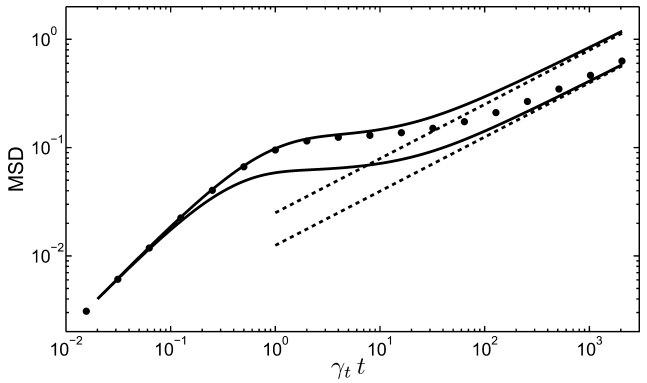

Fig. 6. MSD of the trace particle as a function of time with $c = 0.9$ and $\gamma_d = \gamma_t/100$. Results include solutions to the MC1 (top curves) and MC2 (bottom curves) kinetic equations. Solid lines correspond to numerical solutions, dashed lines correspond to asymptotic solutions, and points correspond to simulation results.

dominant particle jump rate is much smaller than the trace particle jump rate. The MC1 approximation does better at short and intermediate times, whereas the MC2 approximation does better at long times. In general, the MC2 approximation improves as γ_d/γ_t increases.

The improved behavior of the MC2 approximation over the MC1 approximation at long times, both in terms of the MSD and trace correlation function, is a consequence of the fact that the MC1 approximation underestimates the first terms in the expression for $G^{\rm irr}$ at long times. The factor of 2 introduced in the MC2 approximation corrects this exactly at long times, but at the expense of accuracy at short times.

Discussion

The one-dimensional lattice gas is a model of extreme caging that provides unambiguous characteristics, such as the subdiffusive long-time behavior of a tagged particle, against which to test theoretical predictions. This makes the model useful for testing various theoretical approaches intended to describe caging phenomena in liquids.

In this work, we used a diagrammatic kinetic theory to motivate and derive a series of approximations to the irreducible memory function. Each approximation factorizes 4-point time correlation functions into products of 2-point functions and gives a set of kinetic equations that can be solved self-consistently for the trace correlation function.

The mode coupling theory initially presented fails to describe the subdiffusive behavior of a trace particle and thus does not appropriately account for the highly correlated motion induced by persistent caging. We developed a modified mode coupling theory, designated MC1, by combining the focus on disconnected diagrams, which is an ingredient in mode coupling theory, with an exact property of the diagrammatic series for $\chi^{\rm irr}$, the propagator in the irreducible memory function. This apparently minor modification of mode coupling theory predicts subdiffusive behavior of the trace particle at long times, with the correct scaling exponent. A second modified mode coupling theory, designated MC2, was motivated by the form of $\chi^{\rm irr}$ for the case in which the jump rate of the trace particle is zero. It predicts subdiffusive behavior of the trace particle with the correct scaling exponent, and it also gives the correct amplitude of the mean square displacement at long times.

The caging of particles in the one-dimensional model is extreme compared with the effect of caging in higher dimensions, but its effect on the dynamics can be correctly described with simple extensions of the ideas of mode coupling theory. We hope that the graphical methods discussed here can be generalized to develop approximations for the irreducible memory function of more detailed models of liquids in higher dimensions to provide insight into the nature of caging in liquids of small molecules and of polymers. The fact that a simple, graphically motivated generalization of mode coupling theory is so effective in describing caging in one dimension gives some encouragement that this might be a useful approach. Some results along these lines for models of rigid rod polymers have already been obtained (32). We note that, for the present problem, a physically correct theory of caging has been achieved without explicit discussion of dynamic heterogeneity. We hope that the methods of this article can be used as a basis for the theory of 4-point functions that describe dynamic heterogeneity.

Appendix

Numerical Techniques. Numerical solutions to the kinetic equations are obtained at discrete times by applying the time-forward convention for the time derivative of the correlation function: $\partial \hat{C}_t(k,t)/\partial t \approx (\Delta t)^{-1}[\hat{C}_t(k,t+\Delta t) - \hat{C}_t(k,t)]$. The time convolution integrals are computed by using a trapezoidal evaluation rule, and the k-space integral is computed by performing the Fourier transform consistent with a finite lattice with periodic boundary conditions. Since the initial values of the trace correlation function are known, this procedure is well specified.

Asymptotic Techniques. The asymptotic analysis of the MC1 and MC2 equations is carried out in the wavevector-frequency domain, after applying the Laplace transform to the kinetic equations. [The Laplace transform of the trace correlation function is defined as $\hat{C}_t(k,s) = \int_0^\infty dt\, e^{-st}\, \hat{C}_t(k,t)$.] In this domain, the kinetic equations can be written

$$\hat{C}_t(k,s) = \frac{1}{s - (Q_{11}(k) + M(k,s))}$$

$$M(k,s) = 8c(1-c)\gamma_t^2(1-\cos k)\left(\frac{G^{\rm irr}(k,s)}{1 + 4c\gamma_t\, G^{\rm irr}(k,s)}\right)$$

We are interested in the behavior of the trace particle in the hydrodynamic regime, in which $k \ll 1$ and $s \ll 1$, and begin by assuming that $4c\gamma_t\, G^{\rm irr}(k,s) \gg 1$, which can be verified a posteriori. Then

$$M(k,s) \approx 2(1-c)\gamma_t(1-\cos k)\left(1 - \frac{1}{4c\gamma_t\, G^{\rm irr}(k,s)}\right)$$

With use of the exact form of the dominant correlation function, the Laplace transform of the scaled irreducible memory function becomes

$$G^{\rm irr}(k,s) = \frac{\eta}{2}\int_{-\pi}^{\pi}\frac{dk'}{2\pi}\hat{C}_t(k-k', s + 2\gamma_d(1-\cos k')),$$

where $\eta = 1$ and 2 correspond to MC1 and MC2, respectively. The coupled equations above can be combined to give a single integral equation in the unknown function $[M(k,s) + Q_{11}(k)]$. This equation can be solved analytically in the domain in which $k \ll 1$, $s \ll 1$, and $k^2/\sqrt{s} \ll 1$, using a method first outlined by Fedders (3). The solution determines an expression for the correlation function $\hat{C}_t(k,s)$, and inverse Laplace transformation gives the long-time behavior of $\hat{C}_t(k,t)$, for sufficiently small wavevector. The analytic solution in the wavevector-time domain immediately yields an explicit expression for MSD(t) at long times. The results for MC1 and MC2 are presented with the main discussion of the approximations.

Simulation Details. Computer simulations of the dynamic model were performed for one-dimensional systems containing M sites, with periodic boundary conditions and cM particles (M was typically chosen to be 3,200). The initial states for the runs were independently sampled from the equilibrium distribution. For cases with $\gamma_t = \gamma_d$, there was no need to identify one of the particles as a trace particle in performing the simulations. For cases

with $\gamma_t \neq \gamma_d$, one of the particles was identified as a trace particle. The dynamics were calculated by using a standard algorithm for many-particle continuous-time random walk problems. Many statistically independent runs were performed for each condition of interest; the results were used to calculate MSD and correlation functions, as well as their error estimates. The statistical errors are smaller than the size of the data points presented in the figures.

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