

Quantitative test of the mode-coupling theory of the ideal glass transition for a binary Lennard-Jones system

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(Received 5 August 1996)

Using a molecular-dynamics computer simulation we determine the temperature dependence of the partial structure factors for a binary Lennard-Jones system. These structure factors are used as input data to solve numerically the wave-vector-dependent mode-coupling equations in the long-time limit. Using the so-determined solutions, we compare the predictions of mode-coupling theory (MCT) with the results of a previously done molecular-dynamics computer simulation [Phys. Rev. E **51**, 4626 (1995); **52**, 4134 (1995)]. From this comparison we conclude that MCT gives a fair estimate of the critical coupling constant, gives a good estimate of the exponent parameter, predicts the wave-vector dependence of the various nonergodicity parameters very well, except for very large wave vectors, and gives also a very good description of the space dependence of the various critical amplitudes. In an attempt to correct for some of the remaining discrepancies between the theory and the results of the simulation, we investigate two small (*ad hoc*) modifications of the theory. We find that one modification gives worse agreement between theory and simulation, whereas the second one leads to improved agreement. [S1063-651X(97)02301-5]

PACS number(s): 61.43.Fs, 61.20.Ja, 02.70.Ns, 64.70.Pf

I. INTRODUCTION

In the past few years strong evidence was given that for certain types of glass formers *at least* the universal predictions of the so-called mode-coupling theory (MCT) are correct in that it was shown that, e.g., there exists a critical temperature T_c , the factorization property in the β -relaxation regime holds, or two distinct diverging time scales can be observed. An introduction to the theory can be found in some recent review articles [1–3] and in Ref. [4] the reader will find a compendium of many investigations performed to test the validity of the theory. The outcome of most of these tests is that, at least for fragile glass formers, MCT is a valid theory, although recent calculations have shown that the theory might even be applicable to relatively strong glass formers, such as glycerol [5]. Apart from some noticeable exceptions, discussed below, most of the tests done to check the validity of the theory investigated only whether the *universal* predictions of the theory are correct. The reason for this is the fact that the *nonuniversal* predictions of the theory, e.g., the value of T_c or the details of the wave-vector dependence of the nonergodicity parameters, can be tested only for those systems for which the temperature dependence of the structure factor (or of the partial structure factors in the case of a multicomponent system) is known with a fairly high accuracy. Since in most cases these structure factors were not available with the required accuracy, only the universal predictions of the theory could be tested. The drawback with these types of tests is that the various (nonuniversal) parameters occurring in the theory, such as the exponent parameter λ , the critical temperature

T_c , or the nonergodicity parameter $f_c(q)$, had to be considered as fit parameters of the theory, thus making the tests less stringent. There are two exceptions to this. The first one is a system of colloidal particles whose glass transition was studied extensively in light-scattering experiments by Pusey, van Meegen, and Underwood [6]. The structure of such systems is believed to be modeled well by a system of hard spheres. For the structure factor of the latter very reliable analytical expressions are available [7] and thus were used by Götze and Sjögren to demonstrate that in the β -relaxation regime the dynamics of the colloidal particles could be described very well with MCT [8]. Subsequently, Fuchs *et al.* demonstrated that this hard-sphere model is also able to give a good quantitative description of the α relaxation [9,10]. The second system is a model of soft spheres for which Barrat and Latz showed [11] that MCT gives a fair quantitative description of quantities such as the nonergodicity parameter and the critical coupling constant, which were determined by means of computer simulations [12,13]. Thus these two examples show that MCT is able to give not only a *qualitative* correct description of the dynamics of supercooled liquids, but that, *at least* in some cases, it also gives a *quantitative* correct description.

In a recent computer simulation we studied the dynamics of a mixture of Lennard-Jones particles [14–18]. It was shown that at low temperatures the dynamics of this system could be described very well by MCT. However, in these papers only the universal properties of the theory were tested since we used the data from the simulation to fit the occurring parameters of the theory. The goal of the present paper is now to compare the results of the simulation with the predictions of the theory without using any fit parameter at all. The only input to the theory will be the partial structure factors that were obtained from the simulation. In this way it will be possible to make a more stringent test of the theory than it was done in Refs. [14–18] and therefore to test whether also for this system the theory is correct not only in

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a qualitative way but also in a quantitative way.

The rest of the paper is organized as follows. In Sec. II we collect the MCT equations needed to compute the various quantities we investigate. In Sec. III we give the details of the model and of the numerical calculations. In Sec. IV we present our results and in Sec. V we summarize and discuss them.

II. MODE-COUPLING THEORY

In this section we summarize the equations that are necessary to describe the dynamics of the system within the framework of MCT. Most of these equations can also be found in Refs. [11,19–23].

We consider a two-component system of classical particles with particle concentrations x_i and masses m_i , $i=1,2$. In the following the dynamics of the system will be described by means of the partial intermediate scattering functions

$$F_{ij}(q,t) = \langle \delta\rho_i(q,0) \delta\rho_j^*(q,t) \rangle, \quad (1)$$

where $\delta\rho_i(q,t)$ is the density fluctuation for wave vector q at time t of species i . For a binary system it is useful to collect these functions in a 2×2 matrix $\mathbf{F}(q,t)$ with $[\mathbf{F}(q,t)]_{ij} = F_{ij}(q,t)$. The equation of motion of \mathbf{F} is given by

$$\ddot{\mathbf{F}}(q,t) + \mathbf{\Omega}^2(q)\mathbf{F}(q,t) + \int_0^t d\tau \mathbf{M}(q,t-\tau)\dot{\mathbf{F}}(q,\tau) = \mathbf{0}, \quad (2)$$

where the frequency matrix $\mathbf{\Omega}^2$ is given by

$$[\mathbf{\Omega}^2(q)]_{ij} = q^2 k_B T (x_i/m_i) \sum_k \delta_{ik} [\mathbf{S}^{-1}(q)]_{kj}. \quad (3)$$

Here $\mathbf{S}(q)$ stands for the 2×2 matrix consisting of the partial structure factors $S_{ij}(q)$. Within the mode-coupling approximation the memory term \mathbf{M} is given at long times by

$$\begin{aligned} M_{ij}(\mathbf{q},t) &= \frac{k_B T}{2n m_i x_j} \int \frac{d\mathbf{k}}{(2\pi)^3} \\ &\times \sum_{\alpha,\beta} \sum_{\alpha',\beta'} V_{i\alpha\beta}(\mathbf{q},\mathbf{k}) V_{j\alpha'\beta'}(\mathbf{q},\mathbf{q}-\mathbf{k}) \\ &\times F_{\alpha\alpha'}(\mathbf{k},t) F_{\beta\beta'}(\mathbf{q}-\mathbf{k},t), \end{aligned} \quad (4)$$

where n is the particle density, the vertex $V_{i\alpha\beta}(\mathbf{q},\mathbf{k})$ is given by

$$V_{i\alpha\beta}(\mathbf{q},\mathbf{k}) = \frac{\mathbf{q} \cdot \mathbf{k}}{q} \delta_{i\beta} c_{i\alpha}(\mathbf{k}) + \frac{\mathbf{q} \cdot (\mathbf{q}-\mathbf{k})}{q} \delta_{i\alpha} c_{i\beta}(\mathbf{q}-\mathbf{k}), \quad (5)$$

and the matrix of the direct correlation function is defined by

$$c_{ij}(\mathbf{q}) = \frac{\delta_{ij}}{x_i} - [\mathbf{S}^{-1}(\mathbf{q})]_{ij}. \quad (6)$$

Making use of the isotropy of the system, the expression for $M_{ij}(\mathbf{q},t)$ can be reduced to a two dimensional integral:

$$\begin{aligned} M_{ij}(q,t) &= \frac{k_B T}{32n x_j m_i \pi^2 q^3} \int_0^\infty dk k \int_{|q-k|}^{q+k} dp p \\ &\times \sum_{\alpha,\beta} \sum_{\alpha',\beta'} F_{\alpha\alpha'}(q,t) F_{\beta\beta'}(p,t) \\ &\times \{ (q^2 + k^2 - p^2) \delta_{i\beta} c_{i\alpha}(k) + (q^2 + p^2 - k^2) \\ &\times \delta_{i\alpha} c_{i\beta}(p) \} \{ (q^2 + k^2 - p^2) \delta_{j\beta'} c_{j\alpha'}(k) \\ &+ (q^2 + p^2 - k^2) \delta_{j\alpha'} c_{j\beta'}(p) \}. \end{aligned} \quad (7)$$

The memory function for the incoherent intermediate scattering function $F_i^{(s)}$ is given by

$$\begin{aligned} M_i^{(s)}(\mathbf{q},t) &= \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{1}{n} \left(\frac{\mathbf{q} \cdot \mathbf{k}}{q} \right) (cF)_i(\mathbf{k},t) F_i^{(s)}(\mathbf{q}-\mathbf{k},t) \\ &= \frac{1}{16\pi^2 n q^3} \int_0^\infty dk \int_{|q-k|}^{q+k} dp p \{ q^2 + k^2 - p^2 \}^2 \\ &\times (cF)_i(k,t) F_i^{(s)}(p,t), \end{aligned} \quad (8)$$

with

$$\begin{aligned} (cF)_i(k,t) &= [c_{ii}(q)]^2 F_{ii}(q,t) + 2c_{ii}(q)c_{ij}(q)F_{ij}(q,t) \\ &+ [c_{ij}(q)]^2 F_{jj}(q,t), \quad j \neq i. \end{aligned} \quad (9)$$

The matrix of the nonergodicity parameters $\mathbf{f}(\mathbf{q})$ for the coherent intermediate scattering function is given by the solution of Eq. (2) at long times, i.e., $f_{ij}(\mathbf{q}) = \lim_{t \rightarrow \infty} F_{ij}(\mathbf{q},t)$. It can be shown that $\mathbf{f}(\mathbf{q})$ can be computed via the iterative procedure [23]

$$\mathbf{f}^{(l+1)}(q) = \frac{\mathbf{S}(q) \cdot \mathbf{N}[\mathbf{f}^{(l)}, \mathbf{f}^{(l)}](q) \cdot \mathbf{S}(q) + q^{-2} |\mathbf{S}(q)| |\mathbf{N}[\mathbf{f}^{(l)}, \mathbf{f}^{(l)}](q)| \mathbf{S}(q)}{q^2 + \text{Tr}\{\mathbf{S}(q) \cdot \mathbf{N}[\mathbf{f}^{(l)}, \mathbf{f}^{(l)}](q)\} + q^{-2} |\mathbf{S}(q)| |\mathbf{N}[\mathbf{f}^{(l)}, \mathbf{f}^{(l)}](q)|}, \quad (10)$$

where the matrix $\mathbf{N}(q)$ is given by

$$N_{ij}(q) = \frac{m_i}{x_i k_B T} M_{ij}(q). \quad (11)$$

For temperatures above the critical temperature T_c this iteration converges to the trivial solution $\mathbf{f}(q) = \mathbf{0}$ whereas for $T < T_c$ it converges to a nontrivial solution $\mathbf{f}(q) > 0$.

The incoherent nonergodicity parameter $f_i^{(s)}$ can be computed from the iterative procedure

$$q^2 \frac{f_i^{(s,l+1)}(q)}{1 - f_i^{(s,l+1)}(q)} = M_i^{(s)}[\mathbf{f}, f_i^{(s,l)}](q). \quad (12)$$

In order to determine the critical point it is useful to consider the so-called stability matrix \mathbf{C} , which is defined by its action on a vector $\delta\mathbf{f}(q) = (\delta\mathbf{f}_{11}(q), \delta\mathbf{f}_{12}(q), \delta\mathbf{f}_{22}(q))$,

$$(\mathbf{C} \cdot \delta\mathbf{f})(q) = \frac{1}{q^2} [\mathbf{S}(q) - \mathbf{f}(q)] \cdot \{ \mathbf{M}[\mathbf{f}, \delta\mathbf{f}](q) + \mathbf{M}[\delta\mathbf{f}, \mathbf{f}](q) \} \cdot [\mathbf{S}(q) - \mathbf{f}(q)]. \quad (13)$$

We define E_0 to be the largest eigenvalue of this matrix $\mathbf{e}(k) = (e_{11}(k), e_{12}(k), e_{22}(k))$ as the corresponding right and $\hat{\mathbf{e}}(k) = (\hat{e}_{11}(k), \hat{e}_{12}(k), \hat{e}_{22}(k))$ as the corresponding left eigenvector of this matrix. The normalization of these eigenvectors is given by [24]

$$\int_0^\infty dk \sum_{n=11,12,22} \hat{e}_n(k) e_n(k) = 1, \quad (14)$$

$$\int_0^\infty dk \sum_{n=11,12,22} \hat{e}_n(k) [\mathbf{e}(k) \cdot [\mathbf{S}(k) - \mathbf{f}(k)]^{-1} \cdot \mathbf{e}(k)]_n = 1. \quad (15)$$

The critical amplitudes $\mathbf{h}(q) = (h_{11}(q), h_{12}(q), h_{22}(q))$ describe the dynamics of the system in the β -relaxation regime, i.e.,

$$F_{ij}(q, t) = f_{c,ij}(q) + h_{ij}(q) g(t), \quad (16)$$

where $g(t)$ is a function that is independent of q and whose form depends on temperature and the so-called exponent parameter λ , and $f_{c,ij}$ are the nonergodicity parameters at the critical temperature. This critical amplitude is given by the value of the right eigenvector at the critical temperature T_c , i.e.,

$$h_{ij}(q) = e_{c,ij}(q). \quad (17)$$

The value of the mentioned exponent parameter λ is given by

$$\lambda = \int_0^\infty dq \sum_{n=11,12,22} \hat{e}_{c,n}(q) \times \left[\frac{1}{q^2} [\mathbf{S}(q) - \mathbf{f}_c(q)] \cdot \mathbf{M}[\mathbf{e}_c, \mathbf{e}_c] \cdot [\mathbf{S}(q) - \mathbf{f}_c(q)] \right]_n. \quad (18)$$

The procedure to compute the nonergodicity parameters is now the following. Given the partial structure factors for a temperature T that corresponds to the glass state one computes from Eqs. (6) and (7), the memory kernel and iterates Eq. (10) until $\mathbf{f}^{(l)}(q)$ has converged. Then the stability matrix $\mathbf{C}(q)$ and its largest eigenvalue E_0 are computed. It can be shown that in the vicinity of the critical temperature T_c the relation

$$(1 - E_0)^2 = A(T_c - T) + O((T_c - T)^2) \quad (19)$$

holds, which can thus be used for a precise determination of T_c . Having determined T_c , we can compute the right and left eigenvalue of \mathbf{C} at T_c and thus obtain the critical amplitudes $h_{ij}(q)$ and the exponent parameter λ [Eqs. (17) and (18)]. Using the nonergodicity parameters of the coherent intermediate scattering function, we can use Eqs. (8) and (12) to compute finally the nonergodicity parameter for the incoherent intermediate scattering function.

III. MODEL AND COMPUTATIONAL DETAILS

In this section we introduce the system we investigate and give some of the details of our numerical calculations. More details on these calculations can be found in Ref. [26].

The model we are studying is a binary mixture of classical Lennard-Jones particles all of them having mass m . The interaction between two particles of type i and j ($i, j \in \{A, B\}$) is given by $V_{ij}(r) = 4\epsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$. The parameters $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are given by $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, and $\sigma_{BB} = 0.88$. The composition of the mixture is such that $x_A = 0.8$ and $x_B = 0.2$. In the following we will measure length scales in units of σ_{AA} and energy in units of ϵ_{AA} and set $k_B = 1$.

In a recent simulation the dynamics of this system was investigated by means of a molecular-dynamics computer simulation [14–18]. This simulation used 800 particles of type A and 200 particles of type B . The size of the cubic box was held fixed at $L = 9.4$. In order to lower the computational burden the Lennard-Jones potential was truncated and shifted at a distance of $2.5\sigma_{\alpha\beta}$. More details on that simulation can be found in the original papers. In that work also the partial structure factors $S_{ij}(q)$ were calculated. This was done by computing the space Fourier transform of the radial distribution function $g_{ij}(r)$. Because of the finite size of the system this Fourier transform gave rise to unphysical oscillations in the structure factors at small values of q . Since these structure factors are the (only) input in the mode-coupling equations, such unphysical oscillations would possibly modify the outcome of the MCT calculations. Therefore we repeated the simulations and computed the partial structure factor directly from the positions of the particles by means of Eq. (1) and thus avoided the above-mentioned Fourier transform. In order to filter out high-frequency noise in q the so-determined structure factors were smoothed with a spline under tension. Because of the finite size of the box, wave vectors with modulus less than $2\pi/L$ are not accessible. Therefore we extrapolated the determined partial structure factors to $q = 0$.

These new simulations were done only for a few selected values of the temperature, all of them in the vicinity of

the critical temperature, i.e., at $T=1.0$, 0.8 , and 0.6 . For a precise determination of the critical temperature we also needed the structure factors at intermediate values of the temperature. Therefore we used the structure factors at the three mentioned temperatures and a quadratic interpolation scheme to compute the structure factors for intermediate temperatures. Since in this temperature region the structure factors show only a weak variation with temperature, such an interpolation scheme should be fairly reliable. More details on the so-obtained structure factors are given in Sec. IV.

The integral equations presented in Sec. II were solved iteratively in the way described in that section. The occurring integrals were computed using a high-order Simpson scheme. (Note that it is necessary to use an integration scheme that accesses only points that are spaced in an equidistant way since the integrals involve convolutions. Therefore more efficient integration schemes such as Gaussian quadrature cannot be used.) The upper limit of the integrals was set to $q_{co}=40$, which is sufficiently large to allow the direct correlation function to be negligible small for $q > q_{co}$. In order to perform the integration we used 300 grid points in the interval $[0, q_{co}]$. A few calculations with a larger number of points showed that this number is sufficiently large to neglect the dependence of the final results on the used discretisation scheme.

Close to the glass transition the convergence of the iteration scheme given by Eq. (10) was quite slow since the maximum eigenvalue was very close to unity ($1 - E_0 \approx 3 \times 10^{-3}$, which corresponds to $T - T_c \approx 1 \times 10^{-5}$), and only after 1000–2000 iterations reliable results could be obtained. Thus such an iteration took about 24 h on a medium level workstation. Note that in order to get results that are accurate to within 1% it is indeed necessary to determine T_c that precisely, since, e.g., quantities such as the nonergodicity parameters show a square-root dependence on $(T - T_c)$.

IV. RESULTS

In this section we present the obtained results. In the first part we investigate whether MCT, as presented in Sec. II, is able to predict correctly various quantities that are relevant in the dynamics of the supercooled liquid. In the second part we test whether two possible modifications of MCT lead to even better agreement between the theory and the simulation.

The partial structure factors $S_{ij}(q)$, crucial input for the theory, were computed as described in Sec. III. The resulting structure factors are shown in Fig. 1 for $T=1.0$, 0.8 , and 0.6 . [Note that, although in our computation we used $S_{ij}(q)$ for all values of q up to $q_{co}=40$, we show only the range $0 \leq q \leq 20$, since outside this interval the structure factors are almost constant.] From this figures we see that in that range of temperature the dependence of the structure factors on temperature is very smooth, thus justifying the interpolation procedure described in Sec. III to obtain the structure factors at intermediate values of T .

Using the procedure described in Sec. II, we determined the critical temperature T_c to be around 0.922 . This value has to be compared with the result that was obtained from the molecular-dynamics computer simulation, which was $T = 0.435 \pm 0.003$ [14–18]. Thus we find that, for the system

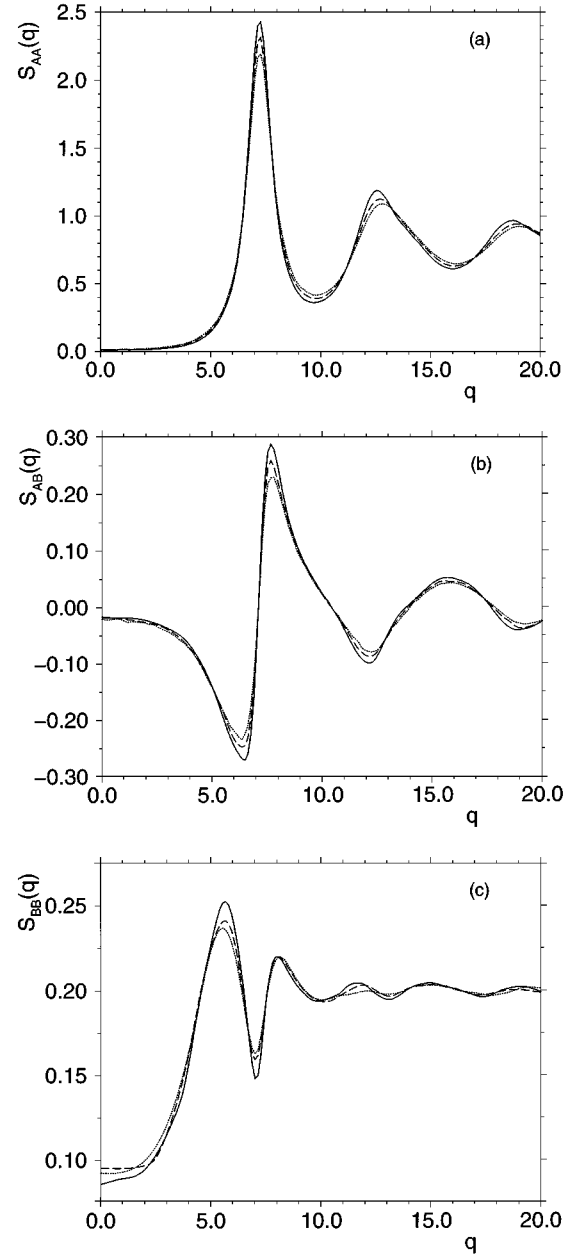


FIG. 1. Partial structure factors for those temperatures used for the interpolation to obtain the partial structure factors at the critical temperature: $T=1.0$ (dotted line), $T=0.8$ (dashed line), and $T=0.6$ (solid line). (a) AA correlation, (b) AB correlation, and (c) BB correlation.

considered here, MCT overestimates the critical temperature by about a factor 2. Since the idealized theory neglects certain types of relaxation processes, which are usually called hopping processes, it can be expected that the critical temperature predicted by the theory is too high. Nevertheless, *at first sight*, the factor 2 seems to be surprisingly large when compared with the results of similar comparisons between the prediction of MCT for the value of the critical coupling parameter and the results of experiments or computer simulations. For example, it was found in light-scattering experiments on colloidal particles, a system that is considered to be described well by a hard-sphere model, that these systems

undergo a glass transition at a packing density ϕ_c that is between 0.56 and 0.58 [6]. This value compares well with the critical packing density of 0.52 ± 0.01 of MCT for a system of hard spheres [27]. Thus, in this case the discrepancy between the experiments and the theory is about 10%. In the case of a binary system of soft spheres, i.e., a pair interaction that is proportional to r^{-12} , it was found by means of computer simulations that the glass transition occurs at a value of the effective coupling constant Γ of 1.46 [12,13]. It can be shown that Γ is the only relevant parameter for the thermodynamic state of such a system and that

$$\Gamma \propto n T^{-1/4}, \quad (20)$$

where n is the particle density. Using the Roger-Young integral equations to compute the structure factors for this system, Barrat and Latz computed the critical value of the coupling constant within the framework of MCT and found it to be 1.32 [11]. Using expression (20) we thus find that the discrepancy is about 10% in the density, comparable to the above-mentioned discrepancy for the hard-sphere system, but about 50% in the critical temperature.

Expression (20) is valid only for a soft-sphere system. However, since at low temperatures it is mainly the repulsive core of the particles that is important for the structure of the liquid, it can be expected that for a Lennard-Jones system, which has the same type of hard core as the soft-sphere system, expression (20) is a reasonable approximation. This expectation is corroborated by the calculations of Bengtzelius in which the critical temperature T_c was determined at different densities for the case of a one-component Lennard-Jones system (the structure factor was computed from the so-called optimized random-phase approximation) [25]. In that work it was shown that a change of 10% in density gives rise to a change of a factor 2 in T_c , in qualitative agreement with the results for the soft-sphere system. Thus we conclude that a discrepancy of a factor 2 in the critical temperature correspond to a discrepancy between theory and simulation of only 20% in the coupling constant, which is comparable to the discrepancy found in the above-mentioned hard-sphere system and the soft-sphere system.

The next quantity for which we compare the prediction of the theory with the result of the computer simulation is the exponent parameter λ . In the simulation this parameter was determined by fitting the functional form provided by MCT for the β correlator [1] to the corresponding master curves found in the β -relaxation regime [16,18]. Depending on the type of correlator investigated, the value of λ was found to vary between 0.75 and 0.83 with the most likely value of $\lambda = 0.78 \pm 0.02$. Our MCT calculations showed that for this system the theory predicts a value of 0.708, which compares quite well with the one found previously in the simulation. The discrepancy in λ between theory and computer simulation is in our case smaller than the one found for the soft-sphere system, for which the theory predicted $\lambda = 0.73$ [11] and for which $\lambda \approx 0.61$ was found in the simulation. This latter value, however, probably has a relatively large error bar, since it was determined from the critical exponent of the diffusion constant close to Γ_c . This critical exponent was determined to be around 2.0 [12,13] and, if it is assumed that the connection predicted by MCT between this critical expo-

nent and the exponent parameter λ holds [1], one obtains the quoted value of λ . However, there are two reasons why the so-determined value of λ might be slightly wrong: First, the value of the critical exponent is not known very precisely [12,13] and, second, it might well be that the above-mentioned connection between the critical exponent for the diffusion constant and the exponent parameter holds only very close to the critical temperature (or coupling parameter). For example, in the simulation of the binary Lennard-Jones system it has been found that the critical exponent for the diffusion constant and the one for the α -relaxation times differ by about 20% [16], although MCT predicts these exponents to be the same. Thus this shows that either the connection proposed by MCT is not always valid or, in order to see the correct critical behavior, one has to be much closer to the critical temperature than it is currently possible with computer simulations (because very close to the critical point the time scales of the α relaxation exceeds the time scale accessible to such simulations). Furthermore, it can be that in the vicinity of T_c the so-called hopping processes become important for the soft-sphere system and thus give rise to an *effective* exponent that is different from the one predicted by the theory. Thus because this connection between the critical exponent of the diffusion constant and the exponent parameter λ is not beyond any doubt, the value of λ in the soft-sphere model is not known very precisely. Finally, we mention that in the comparisons between the prediction of MCT and the results of the experiments on colloidal systems the latter were always assumed to be hard spheres and thus the exponent parameter was not a fit parameter [8].

We now turn our attention to the wave-vector dependence of the nonergodicity parameter. This quantity was determined in the simulation [16] and the results are shown for the coherent intermediate scattering functions for the *AA*, the *AB*, and the *BB* correlation (bold dashed lines), as well as for the incoherent intermediate scattering function for the *A* and the *B* particles in Fig. 2 (thin dashed lines). For small values and very large values of q it was not possible to determine f_c from the simulation because of problems with finite-size effects and statistics. Also included in the figure are the predictions of MCT (solid lines). First we consider Fig. 2(a), which shows $f_c(q)$ for the *AA* correlation and the *A* particles. The first observation is that the theoretical curves match the ones of the simulations qualitatively well for all values of q in that the location of the various extrema in the $f_c(q)$ for the coherent scattering function are reproduced correctly. In addition, the fact that for large values of q the nonergodicity parameter for the coherent scattering function oscillates around the one for the incoherent one is reproduced correctly by the theory.

For wave vectors in the vicinity of the first peak of the structure factor, also the *quantitative* accordance between theory and simulation is very good. This agreement is not as good for wave vectors larger than the second peak in the structure factor. This can be due to two reasons. The first one is that the nonergodicity parameters as determined from the simulation are affected by systematic errors of unknown magnitude [16]. From the way these quantities were measured it can be expected that these errors increase with increasing wave vector, which might be the reason for the increasing discrepancy between simulation and theory. The

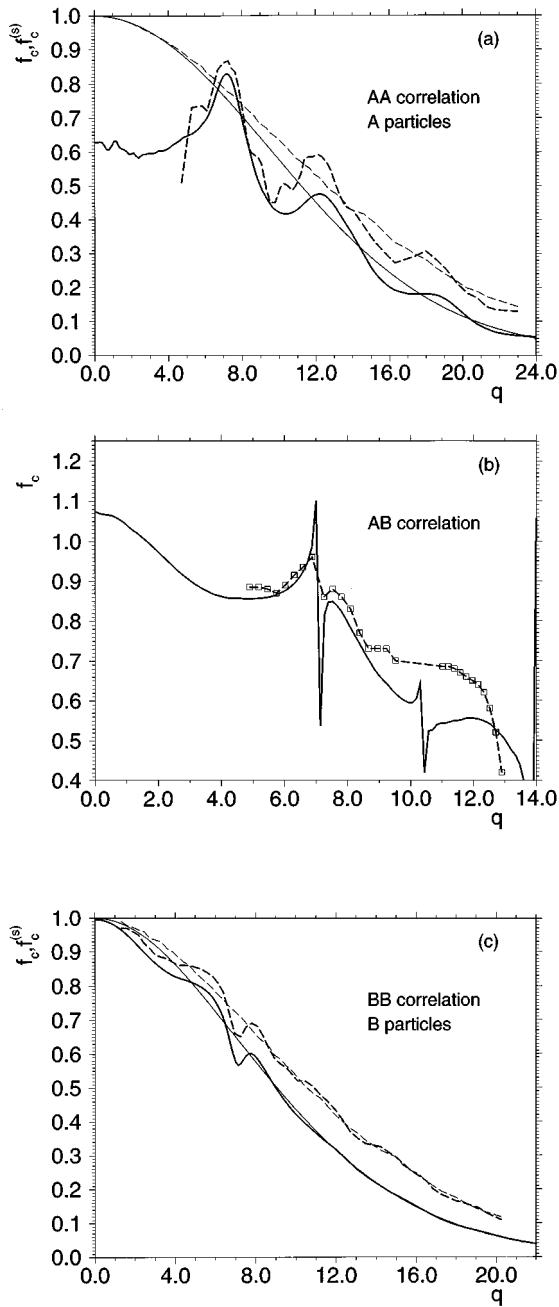


FIG. 2. Nonergodicity parameter $f_c(q)$ for the coherent (bold lines) and incoherent (thin lines) intermediate scattering functions as determined from the simulation (dashed lines) and as predicted by MCT (solid lines). (a) A particles and AA correlation, (b) AB correlation, and (c) B particles and BB correlation.

second possible reason is that for large values of q MCT is no longer reliable. This can be understood as follows. The large wave vectors correspond to distances that are relatively small compared to the diameter of the particles. Now one should remember that in the derivation of the MCT equations a factorization ansatz was made. This ansatz is reasonable for distances on the order of the diameter of a particle, but is likely to be bad for much smaller distances. Thus it is expected that the vertices $V_{i\alpha\beta}$ of Eq. (5) are not quite correct for large values of q or k . Therefore it is not surprising that the accordance between the results of the simulations and the

predictions of MCT is not as good for large values of q as it is for wave vectors in the vicinity of the peak of the structure factor.

Furthermore, we comment on two smaller features in the curves. First, we see that the curve for the nonergodicity parameter for the coherent scattering functions, as computed from the simulation, shows to the left and to the right of the large peaks (at $q \approx 7$ and 12) a small peak. These small peaks are a finite-size effect that is due to the method we computed the intermediate scattering function [16]. Thus the fact that these small peaks are not present at all in the curve as computed from MCT should not be viewed as a failure of the theory to reproduce this feature. Second, we see that the MCT curve for the coherent intermediate scattering function shows some small peaks for wave vectors smaller than 2. This behavior is likely to be due to numerical instabilities in the computation of this curve and therefore has no physical relevance.

The wave-vector dependence of the nonergodicity parameter for the AB correlation is shown in Fig. 2(b). In order to make clear where the measured points actually are, we show them as open squares and the connecting dashed line should be considered just as a guide to the eye. We recognize that this q dependence is very different from the one found for the AA correlation. We see that for values of q near 7 and 10 there is a gap in the data of the simulation. The reason for this is that in the vicinity of these wave vectors the partial structure factor of the AB correlation changes sign, which in turn leads to a singularity and hence to numerical difficulties in determining the corresponding intermediate scattering function. Also included in the figure is the prediction of MCT for this nonergodicity parameter. We see that for intermediate values of q the theoretical curve describes the data very well and we see that MCT correctly predicts the presence of the just-mentioned singular behavior of the nonergodicity parameter. For larger values of q the agreement is only qualitatively correct and the probable reason for this has been given above.

In Fig. 2(c) we show the wave-vector dependence of the nonergodicity parameter for the coherent and incoherent intermediate scattering function for the B particles. From this figure we see that for the coherent part this dependence is very different from the one for the A particles since it resembles much more the q dependence of the incoherent part. This can be qualitatively understood by remembering that the number of B particles is smaller by a factor 5 than the number of A particles. Thus, since the B particles are relatively dilute the coherent intermediate scattering function behaves very similarly to the single-particle correlation function, i.e., the incoherent intermediate scattering function.

As we can see from the figure, MCT is able to reproduce the wave-vector dependence also of these two nonergodicity parameters very well. Although the theoretical curves lie below the ones from the computer simulation for all values of q , the agreement is, nevertheless, on the order of about 5% for intermediate values of q .

From Fig. 2 we recognize that in all cases the nonergodicity parameters as determined from the simulations is a bit larger than the ones predicted by MCT. This is in qualitative agreement with our observation that the critical temperature as found in the simulation is quite a bit lower than the one

predicted by the theory, which can be understood as follows. The nonergodicity parameter is some sort of measure for how much a particle can move in the cage formed by its surrounding particles. Since it can be expected that this movement is smaller the lower the temperature is, it follows that the nonergodicity parameter increases with decreasing temperature. Thus we see that if MCT would have predicted a critical temperature that is lower than the one it predicts now, we would expect that the theoretical nonergodicity parameters would be larger than the ones the theory predicts now. Thus we have evidence that the too high critical temperature and the nonergodicity parameters that are too small are related phenomena. We will return to this point below.

The fact that the predicted nonergodicity parameters are smaller than the ones determined from the simulation motivated us to compare the former with the amplitude of the α relaxation. It should be remembered that in the simulation the nonergodicity parameter was determined from the height of the plateau in the time correlation function. In these simulations it was shown that the height of this plateau is *not* equivalent to the amplitude of the Kohlrausch-Williams-Watts (KWW) function, which describes the relaxation on time scales beyond the β -relaxation time scale, i.e., $\phi(t) = A \exp[-(t/\tau)^\beta]$. Since we have found that this KWW amplitude A is always a bit smaller than the nonergodicity parameter [16,18], a fact that is also corroborated by analytical calculations on the hard-sphere model [9], it is interesting to compare the q dependence of this measured amplitude with the q dependence of the nonergodicity parameter as predicted by MCT. This is done in Fig. 3. We see that for all correlation functions the agreement between these two quantities is very good. To our surprise we find that this agreement is always better than the one between the nonergodicity parameter of the simulation and the one of MCT, which was shown in Fig. 2. (An exception is the AB correlation in the range $5 \leq q \leq 7$, where the experimental point for A are now clearly below the MCT curve.) At the moment it is not clear to us whether this surprising accordance between the KWW amplitude and the nonergodicity parameter of MCT is just a coincidence or whether there is some underlying reason for it. One possibility might be that the corrections to the asymptotic scaling laws of MCT are larger for the β -relaxation regime than for the α -relaxation regime. Thus it would be interesting to compute the full time dependence of the correlation functions within the framework of MCT and to compare the so-obtained results with the results from the simulations. In addition, it would be helpful to make similar comparisons with other systems in order to see whether the just-described phenomenon holds for other systems as well.

The last quantity we investigate is the wave-vector dependence of the critical amplitudes $h(q)$. These amplitudes are used to describe the time dependence of a correlation function in the β -relaxation regime; see Eq. (16). In the computer simulation it was found that in the β -relaxation regime the various intermediate scattering functions are indeed of the form of Eq. (16) [15] in that it was demonstrated that the left-hand side of

$$\frac{\Phi(r,t) - \Phi(r,t')}{\Phi(r',t) - \Phi(r',t')} = \frac{H(r)}{H(r')}, \quad (21)$$

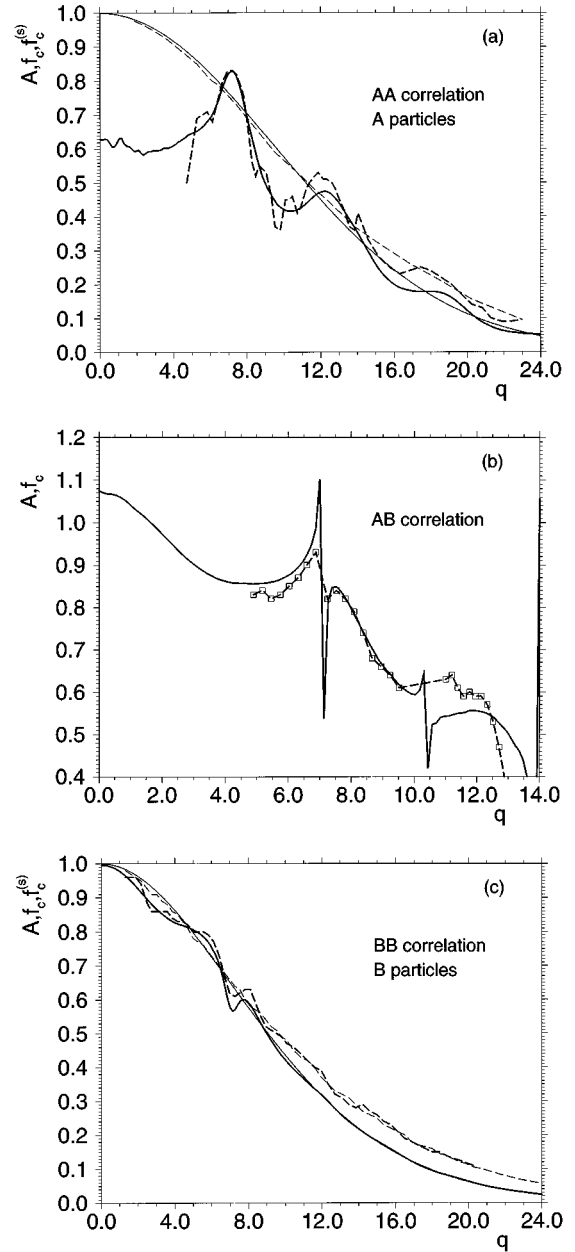


FIG. 3. Kohlrausch-Williams-Watts amplitude A for the coherent (bold lines) and incoherent (thin lines) intermediate scattering functions as determined from the simulation (dashed lines) and nonergodicity parameter as predicted by MCT (solid lines). (a) A particles and AA correlation, (b) AB correlation, (c) B particles and BB correlation.

which is obtained from the space Fourier transform of Eq. (16), holds if the times t and t' are on the time scale of the β relaxation. Here r' can be chosen arbitrarily. From that calculation it was possible to estimate an upper and lower bound for $H(r)$, and these bounds are shown in Fig. 4 for the three coherent intermediate scattering functions (thin solid lines). The value of r' was 1.095, 0.9, and 1.73 for the AA , the AB , and the BB correlation. Also included in the figures are the prediction of MCT for these quantities (bold solid lines). From these figures we recognize that the agreement between the results of the computer simulation and the

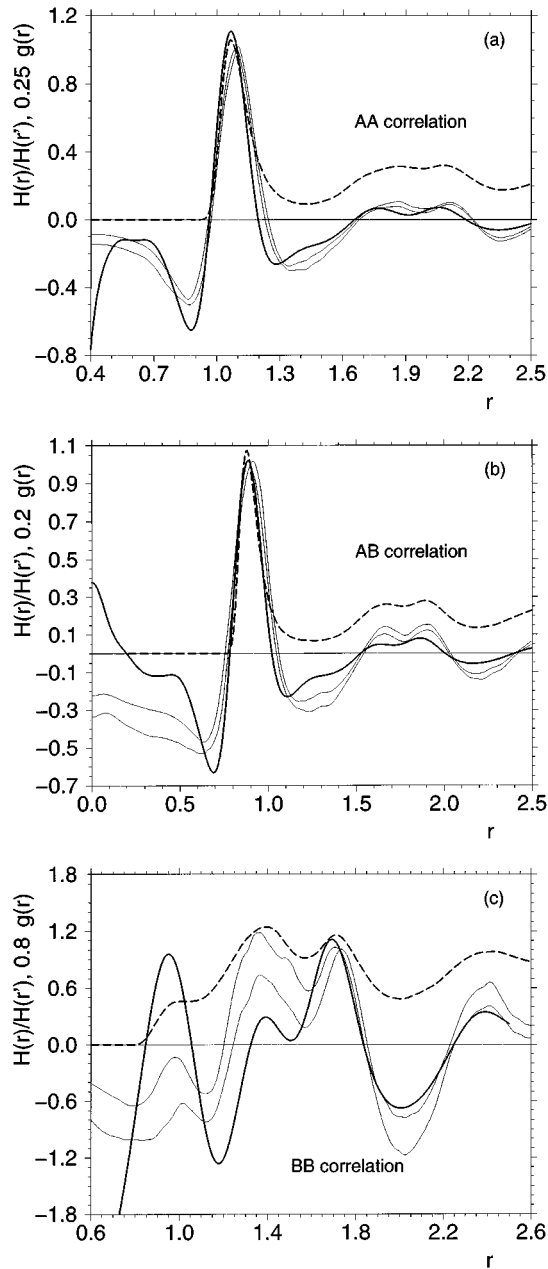


FIG. 4. Critical amplitude $H(r)$ for the coherent intermediate scattering function as predicted by MCT (bold solid line) and the upper and lower bounds for this function (thin lines) as determined from the simulation. The dashed lines are x times the corresponding radial distribution function at $T=0.466$. (a) AA correlation, $x=0.25$; (b) AB correlation, $x=0.2$; and (c) BB correlation, $x=0.8$.

prediction of the theory is, in the case of the AA and the AB correlation, qualitatively as well as quantitatively very good in that also small details in the curves, such as the small dip in the peak at around 1.8, are reproduced correctly. The agreement between simulation and theory is not that good for the case of the BB correlation in that the amplitude of the various peaks is not predicted correctly. However, the position of these peaks is in accordance with the theory and thus MCT is correct for this correlation function at least qualitatively. We also notice that in all three cases the agreement between theory and simulation is not very good at small

distances. This is not surprising, since we have already explained above why MCT is not very accurate for large wave vectors, i.e., small distances.

In order to gain some insight into the nature of the various peaks in $H(r)$ we have included in the figures also the corresponding radial distribution functions $g_{ij}(r)$ at $T=0.466$, the lowest temperature considered in the computer simulation [15] (dashed curves). We see that, for values of r larger than the first nearest-neighbor peak, the different maxima and minima in $H(r)$ occur at the same location at which the corresponding $g_{ij}(r)$ shows its extrema. This means that in q space $h_{ij}(q)$ shows extrema at the same values of q as the corresponding partial structure factor. Since the latter shows a similar q dependence as the corresponding coherent nonergodicity parameter (see Fig. 2), the nonergodicity parameter and $h_{ij}(q)$ will show extrema at the same values of q . A similar observation was made in the case of the soft-sphere system [11] and thus it can be conjectured that this is a general rule.

In the remaining of this section we present the results we obtained by considering two small modification of MCT. These modifications were done in an attempt to improve the agreement between the results of the computer simulation and the prediction of the theory.

The basic idea of the first modification is as follows. In the first part of this section we have shown that MCT is able to give a surprisingly good description of the q dependence of the nonergodicity parameters and the critical amplitudes. The most severe disagreement seems to be that the theory overestimates the critical temperature by quite a bit. Furthermore we have seen that the theory underestimates the nonergodicity parameter and that this disagreement is most pronounced at large values of q . In the discussion of this effect we argued that one of the reason for its occurrence might be that a factorization ansatz, which is used in the derivation of the MCT equations, breaks down for small distances and therefore the MCT equations are not accurate for these values of q . Therefore one could argue that it is better to leave out from the calculation of the memory kernel in Eq. (4) that part of the wave-vector integration altogether, i.e., to restrict the integration to wave vectors with modulus less than a certain limit q_{co} . This approximation is equivalent to the assumption that the structure factor is constant for $q \geq q_{co}$. Thus the value of q_{co} can be used as a fit parameter in order to match the critical temperature as predicted by MCT with the one determined from the simulation. The hope is that this fix of the critical temperature will lead to theoretical nonergodicity parameters that are in better agreement with the ones of the simulation (of course at the cost that for wave vectors larger than q_{co} the theory does not give any nonergodicity parameter at all).

Thus we proceeded as follows. Using the partial structure factors that we determined at $T=0.466, 0.475$, and 0.5 , we made an extrapolation to determine the partial structure factors at $T=0.435$, the value of the critical temperature as determined from the computer simulation. Since at these low temperatures the temperature dependence of the structure factors is only weak and very regular, such an extrapolation is not problematic. Equipped with the structure factors at the correct critical temperature, we determined q_{co} such that the

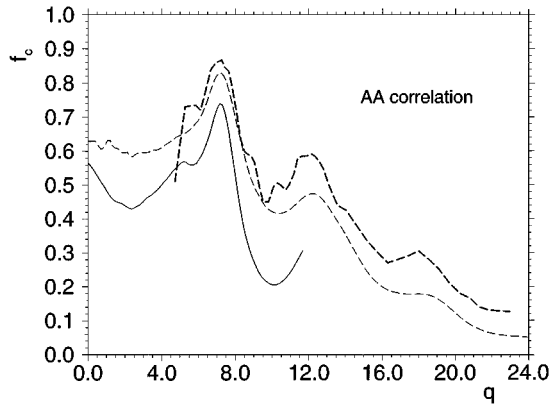


FIG. 5. Nonergodicity parameter for the coherent intermediate scattering function for the AA correlation as determined from the simulation (bold dashed line) and the prediction of MCT for $q_{co} = 11.7$ (solid line) and $q_{co} = 40$ (dashed line).

critical temperature as determined from MCT is exactly at $T = 0.435$, i.e., the critical temperature from the simulation. The value of q_{co} we obtained was around 11.7, i.e., a bit to the right of the first minimum in the partial structure factor for the AA correlation. This value shows, on the one hand, that it is mainly the first peak in the structure factor that is relevant to give a *qualitative* correct description of the transition and, on the other hand, that for a *quantitative* correct calculation of the transition temperature it is necessary to take into account the structure also for larger values of q . With this value of q_{co} we computed the q dependence of the nonergodicity parameters and the result for the AA correlation are shown in Fig. 5 (solid line). Also included is the curve from the simulation (bold dashed line) and, as a reference, the curve when q_{co} is 40, i.e., the value of q_{co} used to compute the results of the first part of this section (thin dashed line). From this figure we recognize that the curve for the new value of q_{co} is now significantly below the curve from the simulation and that the discrepancy between the (modified) theory and simulation is now quite a bit larger than it was with the original theory. Thus this shows two things: first, that the contribution to the memory kernel that come from values of q larger than $q_{co} = 11.7$ are important in order to get quantitatively correct results, despite the above-discussed fact that the integrand is not quite appropriate for such large values of q , and second, that it is not that easy to improve the theory qualitatively by introducing a fit parameter in order to fix certain shortcomings of the theory (e.g., the not so satisfactory prediction of the critical temperature).

The second modification of the theory we did was to ignore the fact that we have to compare the results for the q dependence of the nonergodicity parameter as obtained from the simulation with the prediction of MCT for the nonergodicity parameter *at the critical temperature* T_c . Since we have seen that MCT underestimates the nonergodicity parameters and we know that for temperatures $T < T_c$ the theory predicts that the nonergodicity parameters increase, we tried to correct this discrepancy by computing $f_A^{(s)}(q)$ at a temperature T_{eff} below T_c and to determine T_{eff} by requiring that this nonergodicity parameter, which we will call $f_{eff}^{(s)}$, fits the corresponding quantity from the simulation well. The reason

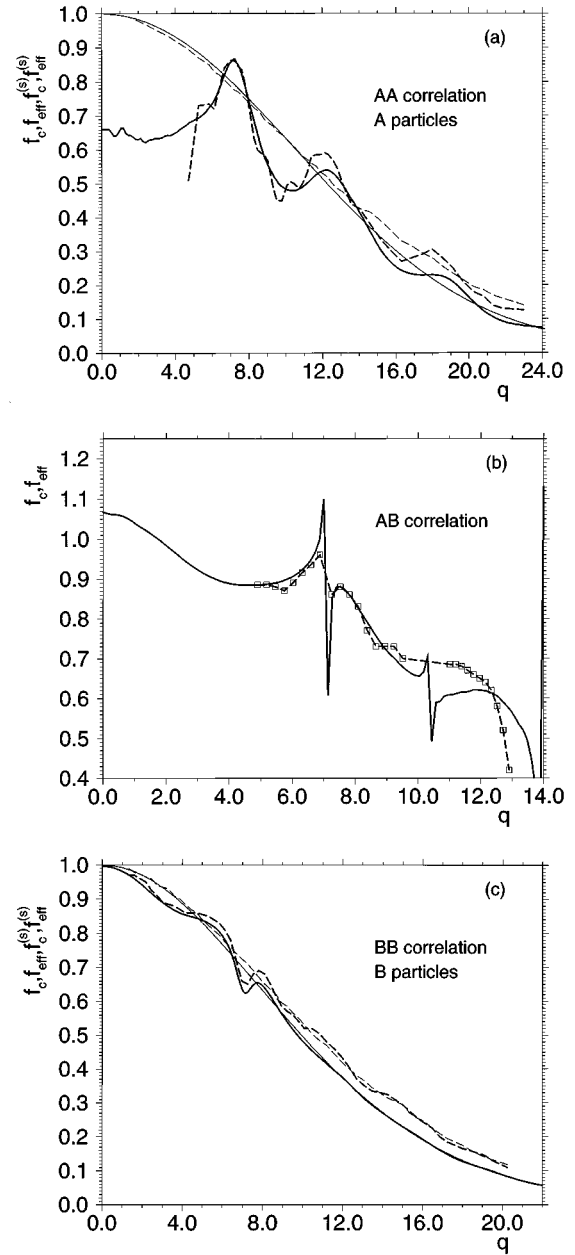


FIG. 6. Nonergodicity parameter $f_c(q)$ for the coherent (bold lines) and incoherent (thin lines) intermediate scattering functions as determined from the simulation (dashed lines). The solid lines are results for the nonergodicity parameter as predicted by MCT for the temperature $T_{eff} = 0.91$. (a) A particles and AA correlation, (b) AB correlation, and (c) B particles and BB correlation.

for choosing this type of nonergodicity parameter, instead of, e.g., the one for the AA correlation, is that in the simulation it can be determined with the best accuracy. This fit gave a value for T_{eff} around 0.91, thus quite close to the original critical temperature $T_c = 0.922$. The resulting q dependence of $f_{eff}^{(s)}$ is shown in Fig. 6(a) together with $f_c^{(s)}$ from the simulation. We see that for small and intermediate values of q the agreement between $f_{eff}^{(s)}$ and $f_c^{(s)}$ is very good. Only for large values of q significant, but not large, discrepancies occur. We also computed the q dependence of the other nonergodicity parameters for the *same temperature* T_{eff} and the results

are shown in Fig. 6. From Fig. 6(a) we see that for the coherent nonergodicity parameter for the AA correlation the agreement between $f_c(q)$ and $f_{\text{eff}}(q)$ has improved significantly compared to the agreement when the original MCT function is used [see Fig. 2(a)] and that for q values in the vicinity of the first peak and the first maximum the agreement is perfect to within the noise of the simulation data. Also for the AB correlation function [Fig. 6(b)] the agreement between simulation and theory has improved considerably compared to the original MCT and the same conclusion holds for the coherent and incoherent nonergodicity parameters for the B particles [Fig. 6(c)]. Thus we conclude that introducing one fit parameter, namely, the temperature T_{eff} at which the nonergodicity parameters are evaluated within the framework of MCT, leads to significant improvement of the agreement between theory and simulation.

V. SUMMARY AND DISCUSSION

We have presented the results of a numerical calculation in which the mode-coupling equations were solved for a binary Lennard-Jones mixture. The goal of these calculations was to test whether the agreement between the predictions of MCT for the dynamics, which was investigated by means of a computer simulation [14–18], holds only for the universal predictions of the theory or also for the nonuniversal ones. Using the partial structure factors, as determined from a computer simulation, as input, we computed within the framework of MCT the critical temperature, the exponent parameter, the q dependence of the various nonergodicity parameters, and the various critical amplitudes. Although the critical temperature as predicted by MCT is a factor 2 larger than the one determined from the computer simulation, we argue that this discrepancy is significantly smaller when expressed through the effective coupling constants and is then comparable with the discrepancies found for this quantity for systems such as hard spheres [6] or soft spheres [11]. The exponent parameter as predicted by the theory is in fair agreement with the one determined from the simulation. MCT makes a very good quantitative prediction for the wave-vector dependence of the nonergodicity parameter for values of q in the vicinity of the first maximum and the first minimum. For large values of q the agreement is still fair and we can rationalize the increasing discrepancy between theory and simulation by arguing that some of the approximations used to derive the mode-coupling equations no longer hold in this limit. In addition, we also showed that the theory is also able to make a quantitatively correct prediction of the various critical amplitudes $H(r)$.

We also compared the q dependence of the Kohlrausch-Williams-Watts amplitude, as determined from the simula-

tion, with the q dependence of the nonergodicity parameter as predicted by MCT and found that the two quantities match surprisingly well. So far it is not clear why this is the case and how general this observation is. Therefore it would be very valuable to make similar comparisons for different types of systems.

In an attempt to improve the agreement between the measured and theoretical nonergodicity parameters we introduced an upper cutoff q_{co} in the integral of the memory kernel and used q_{co} to match the critical temperature T_c between MCT and simulation. We found that the introduction of this fit parameter leads to a worsening of the agreement between the measured and theoretical nonergodicity parameter, which shows that the contributions to the memory kernel from large values of q are important for a quantitative correct description of the nonergodicity parameter. In a second ‘modification’ of the theory we used temperature as a fit parameter and determined a temperature $T_{\text{eff}} < T_c$ such that the resulting incoherent nonergodicity parameter for the A particles fits the simulation data well. We found that at this temperature also all the other nonergodicity parameters fit the data from the simulation well, in some cases even very well. Thus it seems that there exists a temperature T_{eff} for which MCT is able to predict very well the q dependence of the various nonergodicity parameters as measured in the simulation at T_c . This shows that the intrinsic structure of the mode-coupling equations are clearly able to correctly describe such quantities and that it is perhaps only through the omission of certain contributions to the memory kernel that there is no perfect quantitative agreement between the prediction of the theory and the results of the simulation.

To summarize, we can say that our calculations have shown that MCT is able to give a correct *quantitative* description of the dynamics of a simple liquid if one restricts oneself to quantities such as the critical temperature, the exponent parameter, the nonergodicity parameter, or the critical amplitudes. Whether MCT is also able to give a correct description of the *full* time dependence of the various correlation functions, as it is the case for the β -relaxation regime in colloidal systems [8], remains to be tested and is the subject of ongoing work.

ACKNOWLEDGMENTS

We thank M. Fuchs for extensive help and enlightening discussions during this work, W. Götze for valuable discussions and useful comments on the manuscript, K. Binder for helpful comments on the manuscript, and J. L. Barrat for providing us with some programs that allowed to check our programs. This work was supported by SFB 262/D1 of the Deutsche Forschungsgemeinschaft.

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