Metastable dynamics of the hard-sphere system

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The reformulation of the mode-coupling theory (MCT) of the liquid-glass transition which incorporates the element of metastability is applied to the hard-sphere system. It is shown that the glass transition in this system is not a sharp one at the special value of the density or the packing fraction, which is in contrast to the prediction by the conventional MCT. Instead we find that the slowing down of the dynamics occurs over a range of values of the packing fraction. Consequently, the exponents governing the sequence of time relaxations in the intermediate time regime are given as functions of the packing fraction, with one additional parameter that describes the overall scale of the metastable potential energy for defects in the hard-sphere system. Implications of the present model on the recent experiments on colloidal systems are also discussed.

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I. INTRODUCTION

In Refs. [1,2], the notion of metastability was used in the reformulation of the mode-coupling theory (MCT) [3,4] of the liquid-glass transition. It was shown that the temperature dependence of the transition is smooth, as observed in recent experiments [5,6], showing no evidence for the special transition temperature conventionally assumed in MCT. In this paper, we apply the basic picture obtained in Refs. [1,2] to a more realistic situation by considering the effects of the structure of supercooled liquids on the slowing down of the dynamics. For a simple system like hard-sphere fluids considered here, we find that the observed slowing down of the dynamics occurs over a range of values of the packing fraction. This is in contrast to the prediction by the conventional MCT [7] that there exists a critical packing fraction for the transition. Consequently, we find that the exponent parameters describing the relaxation sequence in the intermediate time regime are given as smooth functions of the packing fraction with one additional parameter, which is related to the existence of metastable defects in the system.

Much of the recent theoretical progress on the liquid-glass transition problem has been inspired by the MCT [3,4]. It was particularly successful in explaining the very elaborate sequence of time relaxations which has been observed in many experiments [8,9]. The conventional interpretation of this theory assumes a sharp transition as the system approaches the critical temperature or the critical density. Although the sharp nature of the transition is smeared by the cutoff effect [10], the notion of a critical temperature or density at which the dynamics is arrested still remains in the theory [11]. For example, the exponents governing the time relaxations are defined only at that particular temperature or density. This is, however, incompatible with the recent experimental results [5] showing a more universal behavior and smooth temperature dependences. Other recent experiments [6] also indicate that the exisitence of the well-defined transition temperature is very doubtful.

The basic ingredient in the reformulation of MCT in Refs. [1,2] is the introduction of the metastable defect variable and its coupling to the density fluctuations in the glass transition problem. The defect variable is supposed to be governed by a very long time scale compared to the mass density and the metastability is incorporated through a double-well-type potential energy for the defect variable. By investigating the conditions that the defect variable must satisfy in order to be on the critical surface associated with MCT [12], the authors of Ref. [1] were able to obtain the observed slowing down without having to adjust the temperature. The condition for slowing down is given instead by a self-consistent condition between the low activation barrier for defects and its weak coupling to the density fluctuation [1,2]. The temperature dependence of the parameters describing the metastable potential for defects turns out to be smooth. The exponents for the time relaxation sequences can be determined for a range of temperatures showing a smooth temperature dependence compatible with recent experiments.

In the analysis of those models, however, the wave-number dependences were suppressed as a simplifying assumption. The static structure factor for the density fluctuation $S(q)$ was treated in a very simple manner by assuming that it is constant for $q < \Lambda$ and zero otherwise, where Λ is the large wave-number cutoff. In this paper, we generalize the previous model by considering a model where the structure factor has a more realistic wave-number dependence. We focus here on the dynamics of hard-sphere fluids for which an accurate approximate analytical treatment of $S(q)$ is available. We restrict our analysis here to the intermediate time regime before the primary relaxation where much of the analysis can be carried out analytically. A detailed MCT analy-

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sis has been carried out in Ref. [13] for this time regime, which is very useful in our analysis here. We note that in the previous model [1,2] the temperature was represented by the parameter ξ which is proportional to Λ^3 as well as to the temperature. The appearance of the large wave-number cutoff in the temperature parameter ξ is directly related to the suppression of the wave-number dependence in the model. When one considers the wave-number dependence of $S(q)$, however, we find that the role played by ξ in the previous case is replaced, in the case of hard-sphere fluids, by the more physical parameter, the packing fraction.

The model in Refs. [1,2] is based on the fluctuating nonlinear hydrodynamics (FNH) for a set of slow variables consisting of the mass density $\rho(\mathbf{x})$, the momentum density $\mathbf{g}(\mathbf{x})$, and the defect density $n_d(\mathbf{x})$. In a rigorous hydrodynamic description of crystalline solids, one would be forced to include the defect density variable [14,15] along with Nambu-Goldstone modes due to the broken translational invariance. In a dense amorphous system, although there is no broken continuous symmetry, one can consider a situation where this variable plays a role in the hydrodynamic description of the system [16]. In this paper, we do not construct $n_d(\mathbf{x})$ from a microscopic definition. The only information we need is that the defect density is a scalar variable interacting weakly with the mass density and that it is metastable in the sense that the potential energy $h(n_d)$ for n_d satisfies $h'(\bar{n}_d) = 0$ for some $\bar{n}_d$.

As discussed in Ref. [17], the wave-number dependence can be incorporated into the FNH formulation through the terms in the effective Hamiltonian F that contains spatial derivatives of the variables. More generally, one can include terms where the coefficients depend explicitly on the position $\mathbf{x}$. We construct F such that the terms that depend on the density fluctuation $\delta\rho$ yield the correct static structure factor $S(q)$ for the hard-sphere system, where $\delta\rho = \rho - \rho_0$ with the average mass density ρ_0. In the presence of the defect variable, we must also consider the effect of the defect structure on the dynamical slowing down. Unfortunately, a microscopic description for the structure factors in the presence of defects is not available even for a simple system like a hard-sphere fluid. We assume here that the local behavior of defects is similar to that of particles. Thus we assume that any possible effect of the defect structure is reflected in the coupling term in F between the density fluctuation and the defect fluctuation δn_d, where $\delta n_d \approx n_d - \bar{n}_d$ [18] with the metastable defect density $\bar{n}_d$. This assumption is reasonable since a vacancy is created whenever a particle moves to a different position to make an interstitial. In this paper we assume, as a first approximation, that the coupling term in F between $\delta\rho$ and δn_d has the same spatial form as the term quadratic in $\delta\rho$. As we shall see below, this corresponds to choosing the static defect-density correlation function to be proportional to $s(q)-1$, where $s(q) = S(q)/(m\rho_0)$ is the dimensionless form of the structure factor $S(q)$ with m the mass of the particle. This quantity is just the static structure factor for the density fluctuation excluding the self-correlation effect. The potential energy for n_d is chosen to have the same double well potential as in Refs. [1,2]. The basic picture of Refs. [1,2] is then retained in the sense that the slowing down of the dynamics corresponds to the limit of the low activation barrier for defects and the weak coupling.

As mentioned above, MCT successfully explains the observed sequence of time relaxations. This sequence can be summarized as follows: After the microscopic time scale, the system goes into the intermediate time regime where the density autocorrelation function $\phi(t)$ exhibits the power-law decay, $\phi \sim f + A_1 t^{-a}$, followed by the von-Schweidler relaxation, $\phi \sim f - A_2 t^b$. The system then crosses over to the primary (α) relaxation regime which can be described by a stretched exponential decay $\phi \sim \exp\{(t/\tau_\alpha)^\beta\}$.

In the intermediate time regime, a detailed analysis is available [13] for the general MCT equations including the wave-number dependence. It is shown there that all microscopic structural details are summarized into one exponent parameter λ, which gives the power-law and the von-Schweidler exponents a and b. Thus, given a microscopic model, the corresponding λ can be calculated. In the present case, we find, assuming the system is on the critical surface, that λ depends upon the parameter describing the overall scale of the metastable potential for defects as well as on the packing fraction. This result that the exponent parameter λ is given as a function of the packing fraction is conceptually very different from the results of the earlier MCT calculations on the hard-sphere system [7,19–21], where only the simplest contribution from the density fluctuation to the dynamic viscosity is taken into account. In those cases, the transition is controlled by the packing fraction and thus λ is defined only at the critical packing fraction just as in a second-order phase transition. According to the picture presented here, the transition can take place over a range of packing fractions with different values of the exponents.

In Sec. II, we construct the FNH model including the wave-number dependence and present the relevant results to our discussion of the slowing down of the dynamics. Since the calculation follows closely those in Refs. [1,2] for the wave-number-independent model, we emphasize here only the important results. In Sec. III, we present the results of numerical analysis of the model. In Sec. IV, we conclude with a brief discussion.

II. MODEL

The FNH approach developed in Refs. [1,2] is based on the generalized Langevin equations for the slow variables, $\{\rho, \mathbf{g}, n_d\}$. As mentioned in the preceding section, the wave-number dependence can be implemented through general spatially varying coefficients of terms in the effective Hamiltonian $F[\rho, \mathbf{g}, n_d]$, which governs the static property. In the present model, F is given by

$$F[\rho, \mathbf{g}, n_d] = F_K[\delta\rho, \mathbf{g}] + F_u[\delta\rho] + F_c[\delta\rho, n_d] + F_v[n_d]. \tag{2.1}$$

Here F_K is the usual kinetic energy term $F_K[\rho, \mathbf{g}] =$

$\int d^3\mathbf{x}\ \mathbf{g}^2/(2\rho)$. For the terms that are dependent on the density fluctuation only, we take the Ramakrishnan-Yussouff form [22]

$$F_u[\delta\rho] = \frac{k_BT}{m}\int d^3\mathbf{x}\ \left[\rho\ln\frac{\rho}{\rho_0} - \delta\rho\right] - \frac{k_BT}{2m^2} \times \int d^3\mathbf{x}d^3\mathbf{x}'\ \delta\rho(\mathbf{x})C(\mathbf{x}-\mathbf{x}')\delta\rho(\mathbf{x}'), \quad (2.2)$$

where k_BT is the temperature, m is the mass, and $C(x)$ is the Ornstein-Zernike direct correlation function for the density fluctuation [23]. For the coupling term, we have in general

$$F_c[\delta\rho, n_d] = \int d^3\mathbf{x}d^3\mathbf{x}'\ n_d(\mathbf{x})B(\mathbf{x}-\mathbf{x}')\delta\rho(\mathbf{x}') \quad (2.3)$$

for some function $B(\mathbf{x})$ to be specified later. Equation (2.3) is the simplest coupling term between two scalar variables. We write the Fourier transform of $B(\mathbf{x})$ as $B(\mathbf{q}) \equiv \int d^3\mathbf{x}\exp(i\mathbf{q}\mathbf{x})B(\mathbf{x}) \equiv Bb(q)$, where the constant B represents a scale of the coupling energy with the appropriate dimension for $B(q)$ and the dimensionless $b(q)$ contains the wave-number dependence of $B(q)$. In Eq. (2.1), the potential-energy part $F_v[n_d]$ for n_d is given by the same double-well potential $h(n_d)$ with the metastable defect density $\bar{n}_d$ as in Refs. [1,2]: $F_v[n_d] = \int d^3\mathbf{x}\ h(n_d)$. In fact, one can take a general form for $h(n_d)$ which satisfies $h'(\bar{n}_d) = 0$. Then the potential energy is described by the parameters $\mu \equiv \bar{n}_d^2 h''(\bar{n}_d)$ and $\nu \equiv \bar{n}_d^3 h'''(\bar{n}_d)$. We note that, if $\mu \to 0$, the potential $h(n_d)$ develops an inflection point at $n = \bar{n}_d$, which corresponds to the potential with very shallow metastable wells and low activation barriers for the defects.

The static correlation functions can readily be found from Eq. (2.1):

$$\langle\delta\rho(\mathbf{q})\delta\rho(-\mathbf{q})\rangle \equiv S(q) = \frac{m^2n_0}{1-n_0C(q)}, \quad (2.4a)$$

$$\langle\delta\rho(\mathbf{q})\delta n(-\mathbf{q})\rangle = -\frac{B}{h''(\bar{n}_d)}S(q)b(q), \quad (2.4b)$$

$$\langle\delta n(\mathbf{q})\delta n(-\mathbf{q})\rangle = \frac{k_BT}{h''(\bar{n}_d)}, \quad (2.4c)$$

where $n_0 \equiv \rho_0/m$ is the average number density. The first equation reproduces the correct relation between the static structure factor $s(q)$ and the direct correlation function $C(q)$. In calculating Eq. (2.4), we neglected the terms of order B^2/μ compared to those of order B/μ, which is consistent with the self-consistent condition obtained in Ref. [1] for the slowing down of the dynamics: The slowing down corresponds to a weak coupling ($B \to 0$) and a shallow metastable well for defects ($\mu \to 0$) with the condition $B \sim \mu^2$. As indicated in Sec. I, the coupling energy term is constructed such that the static defect-density correlation function behaves like $s(q) - 1$. This is achieved in Eq. (2.4) by taking

$$b(q) = -n_0C(q). \quad (2.5)$$

As one can see from Eqs. (2.2), (2.3), and (2.5), the coupling term F_c has the same form as the quadratic interaction term between the density fluctuations.

The construction of the generalized Langevin equations for a general set of slow variables is described in Ref. [24]. The main ingredients in the construction are the effective Hamiltonian and the Poisson brackets between the slow variables which are related to the streaming velocities governing the reversible dynamics. In the present case, the set of slow variables is given by $\{\rho, \mathbf{g}, n_d\}$ with the effective Hamiltonian, Eq. (2.1). The Poisson brackets involving the defect density n_d are taken to have the same structure as those involving ρ, since n_d is a scalar quantity. The calculation of the Langevin equations in this case from the effective Hamiltonian Eq. (2.1) is a straightforward generalization of the wave-number-independent case described in Refs. [1,2]. The final expressions for the Langevin equations, however, are quite complicated due to the presence of the spatially varying coefficients in the effective Hamiltonian, which will not be presented here. One can put those equations into the field-theoretic formalism of Martin-Siggia-Rose [25], which allows one to systematically calculate the nonlinear corrrections to the Gaussian response and correlation functions. The detailed calulation of the nonlinear corrections relevant to the glass transition problem also follows closely the wave-number-independent case and the reader is referred to Refs. [1,2].

In the framework of MCT, nonlinear couplings between density fluctuations in the dynamic viscosity are responsible for the dynamical slowing down. This mechanism is most easily seen through the normalized density autocorrelation function:

$$\phi(\mathbf{q},t) = \langle\delta\rho(\mathbf{q},t)\delta\rho(-\mathbf{q},0)\rangle/S(q). \quad (2.6)$$

The Laplace transform of $\phi(\mathbf{q},t)$, defined by $\phi(\mathbf{q},z) = -i\int_0^\infty dt\exp(izt)\phi(\mathbf{q},t)$, is represented as

$$\phi(\mathbf{q},z) = \frac{\rho z + iq^2\Gamma(\mathbf{q},z)}{\rho[z^2-\Omega_0^2(q)] + izq^2\Gamma(\mathbf{q},z)}, \quad (2.7)$$

where $\Omega_0^2(q)$ is the microscopic phonon frequency and $\Gamma(\mathbf{q},z)$ is the renormalized dynamic viscosity.

As discussed in Sec. I, MCT predicts that $\phi(\mathbf{q},t)$, as a function of time, exhibits a very elaborate relaxation sequence. As a first step, we restrict the present analysis to the intermediate time regime where the MCT analysis is significantly simplified in the following aspects. As shown in Ref. [13], all the structural details of the system in the intermediate time regime can be described by a single number λ which is related to the power-law and the von-Schweidler exponents a and b in the usual way [12]:

$$\frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \lambda = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)}, \quad (2.8)$$

where Γ denotes the gamma function. Consequently, a and b are wave-number independent, while all the other parameters describing the time relaxation sequence depend on the wave number. Also, in the intermediate time regime, the defect autocorrelation function can be

regarded as a constant in time due to its extremely long time scale [2]: $\langle \delta n(\mathbf{q},t)\delta n(-\mathbf{q},0)\rangle = k_BT/h''(\bar{n}_d)$. Thus, the analysis of the system in the α-relaxation regime must include the time dependence of the defect autocorrelation function as was analyzed in the wave-number-independent case in Ref. [2]. In the intermediate time regime, this kind of complication does not occur and the renormalized viscosity can be expressed in terms of the density autocorrelation function alone.

For the calculation of the nonlinear contribution to $\Gamma(\mathbf{q},z)$, we follow the field-theoretic calculation in Ref. [2]. We find, in the time regime before the primary α relaxation, the dynamic viscosity is represented by

$$\Gamma(\mathbf{q},z) = \Gamma_0 + \int_0^\infty dt\, e^{izt} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \times\Big[V^{(1)}(\mathbf{q},\mathbf{k})\phi(\mathbf{k},t) + V^{(2)}(\mathbf{q},\mathbf{k})\phi(\mathbf{k},t)\phi(\mathbf{q}-\mathbf{k},t)\Big], \tag{2.9}$$

where $V^{(1)}$ and $V^{(2)}$ are appropriate vertices to be evaluated and Γ_0 is the bare viscosity governing the microscopic dynamics. The appearance of the term linear in $\phi(\mathbf{k},t)$ in Eq. (2.9) is a direct consequence of the constant defect autocorrelation function in this time regime [26].

The vertices $V^{(1)}$ and $V^{(2)}$ depend on the coupling constant B and the parameters μ,ν describing the metastable potential $h(n_d)$ for defects. The basic picture obtained in Ref. [1] is that the slowing down corresponds to the weak coupling ($B \to 0$) and the low activation barrier ($\mu \to 0$) limit with the condition $B \sim \mu^2$. In this limit, the vertices are completely described by the average number density n_0 and the following two dimensionless parameters:

$$y \equiv \frac{1}{n_0}\frac{\nu}{k_BT}, \qquad \kappa \equiv \nu^2\frac{x}{\mu^2}, \tag{2.10}$$

where $x \equiv (B\rho_0\bar{n}_d)/(n_0k_BT)$ is the dimensionless parameter describing the scale of the coupling energy. We recall that ν is the parameter proportional to the third derivative of $h(n_d)$ at $n_d = \bar{n}_d$. Thus, when the second derivative $\mu \to 0$, the parameter y just represents the overall scale of the double-well potential. The parameter κ is the appropriate ratio between the weak coupling (x) and the low barrier (μ^2) for defects. We find that for the effective Hamiltonian, Eq. (2.1), the vertices are given by

$$V^{(1)}(\mathbf{q},\mathbf{k}) = \frac{s(\mathbf{q})}{n_0}\Big[2y\frac{1}{q}U(\mathbf{q},\mathbf{k})s(\mathbf{k})s(\mathbf{q}-\mathbf{k}) + \kappa n_0 C(\mathbf{k})s(\mathbf{k})\Big] + O(\mu) \tag{2.11a}$$

$$V^{(2)}(\mathbf{q},\mathbf{k}) = \frac{s(\mathbf{q})}{n_0}\Big[\frac{1}{2q^2}U^2(\mathbf{q},\mathbf{k}) - y\frac{1}{q}U(\mathbf{q},\mathbf{k})\Big]s(\mathbf{k})s(\mathbf{q}-\mathbf{k}) + O(\mu), \tag{2.11b}$$

where

$$U(\mathbf{q},\mathbf{k}) \equiv \frac{1}{q}\Big[(\mathbf{q}\cdot\mathbf{k})n_0C(\mathbf{k}) + [\mathbf{q}\cdot(\mathbf{q}-\mathbf{k})]n_0C(\mathbf{q}-\mathbf{k})\Big]. \tag{2.12}$$

We note that in the previous MCT studies of hard-sphere fluids [7,19–21] only the quadratic contribution ($V^{(2)}$) with the first term in Eq. (2.11b) was considered, which corresponds to the case where $y = \kappa = 0$ in this model.

III. ANALYSIS OF THE MODEL

Equations (2.7) and (2.9) with the vertices Eq. (2.11) completely specify our model which incorporates the wave-number dependence of the system. In this section, we apply the model to the case of a hard-sphere fluid using a known approximate but realistic hard-sphere structure factor.

A. Basic equations from the general MCT analysis

We first discuss the relevant results from the detailed MCT treatment [13] of Eqs. (2.7) and (2.9) for a general set of vertices $V^{(i)}, i = 1,2,...,M$. It was found that the microscopic structural details of the system are summarized into a single parameter λ. This parameter is related to the the power-law and von-Schweidler exponents $a > 0$ and $b > 0$ via Eq. (2.8). The MCT analysis of the coupled set of equations (2.7) and (2.9) indicates an ergodic-nonergodic-type transition as parameters describing the vertices approach critical values. The nonergodic phase is characterized by $\phi(\mathbf{q},t \to \infty) = f(\mathbf{q})$ with $f(\mathbf{q}) > 0$. In the present case where $M = 2$, the nonergodicity parameter $f(\mathbf{q})$ is given as a nonvanishing solution of

$$\frac{f(\mathbf{q})}{1-f(\mathbf{q})} = \int \frac{d^3\mathbf{k}}{(2\pi)^3}\Big[V^{(1)}(\mathbf{q},\mathbf{k})f(\mathbf{k}) + V^{(2)}(\mathbf{q},\mathbf{k})f(\mathbf{k})f(\mathbf{q}-\mathbf{k})\Big], \tag{3.1}$$

while in the ergodic phase, only the trivial solution $f(q) = 0$ to Eq. (3.1) can be found. The exponent parameter λ is determined for the critical values of the parameters by

$$\lambda = \int \frac{d^3\mathbf{q}}{(2\pi)^3}\int \frac{d^3\mathbf{k}}{(2\pi)^3}\hat{e}_c(\mathbf{q})V^{(2)}(\mathbf{q},\mathbf{k})[1-f_c(\mathbf{k})]^2 \times[1-f_c(\mathbf{q}-\mathbf{k})]^2 e_c(\mathbf{k})e_c(\mathbf{q}-\mathbf{k}), \tag{3.2}$$

where $e_c(\mathbf{k})$ and $\hat{e}_c(\mathbf{k})$ are left and right eigenvectors of

$$W(\mathbf{q},\mathbf{k}) = [1-f_c(\mathbf{k})]^2\Big[V^{(1)}(\mathbf{q},\mathbf{k}) + 2V^{(2)}(\mathbf{q},\mathbf{k})f_c(\mathbf{q}-\mathbf{k})\Big], \tag{3.3}$$

$$\int \frac{d^3\mathbf{k}}{(2\pi)^3}W(\mathbf{q},\mathbf{k})e_c(\mathbf{k}) = e_c(\mathbf{q}), \qquad \int \frac{d^3\mathbf{q}}{(2\pi)^3}\hat{e}_c(\mathbf{q})W(\mathbf{q},\mathbf{k}) = \hat{e}_c(\mathbf{k}) \tag{3.4}$$

with the normalization $1 = \int d^3\mathbf{k}/(2\pi)^3 \hat{e}_c(\mathbf{k}) e_c(\mathbf{k}) = \int d^3\mathbf{k}/(2\pi)^3 \hat{e}_c(\mathbf{k}) e_c^2(\mathbf{k})[1 - f_c(\mathbf{k})]$.

As mentioned in the preceding section, MCT predicts a two-step relaxation process in the intermediate time regime. After the microscopic time scale τ_0, the normalized density autocorrelation function $\phi(\mathbf{q}, t)$ shows the power-law decay which can be described as [20,27]

$$\phi(\mathbf{q}, t) = f_c(q) + h(q) c_\epsilon \left(\frac{t}{\tau_a}\right)^{-a}. \tag{3.5}$$

This is valid for the time regime $\tau_0 \ll t \ll \tau_a$, where the characteristic time scale is given by

$$\tau_a \sim |\epsilon|^{-\frac{1}{2a}}. \tag{3.6}$$

Here ϵ is the control parameter indicating how far the system is from the transition and thus the ideal glass transition corresponds to $\epsilon = 0$. In Eq. (3.5), the coefficients are given by $c_\epsilon = \sqrt{|\epsilon|}$ and $h(q) = [1 - f_c(q)]^2 e_c(q)$. For longer times $t \gg \tau_a$, the system undergoes the von-Schweidler relaxation if $\epsilon < 0$,

$$\phi(\mathbf{q}, t) = f_c(q) - h(q) A_2 \left(\frac{t}{\tau_\alpha}\right)^b \tag{3.7}$$

with a positive constant A_2. This mechanism is valid for the time scale $\tau_a \ll t \ll \tau_\alpha$ before the α relaxation, where the characteristic time scale for the α relaxation is given by

$$\tau_\alpha \sim |\epsilon|^{-\gamma}, \qquad \gamma = \frac{1}{2a} + \frac{1}{2b}. \tag{3.8}$$

For $\epsilon > 0$, $\phi(\mathbf{q}, t)$ decays to a constant, $f(q) = f_c(q) + h(q) c_\epsilon / \sqrt{1 - \lambda}$. We note that the critical nonergodicity parameter $f_c(q)$ and the coefficient $h(q)$ do not depend on the control parameter ϵ.

B. Analysis for a hard-sphere fluid

We calculate the vertices given by Eq. (2.11), using the Perkus-Yevick solution [23] for the hard-sphere structure factor, $s(q\sigma)$, with the Verlet-Weiss correction [28], where σ is the sphere diameter. For this system, it is more convenient to use the packing fraction η instead of the average number density n_0, where $\eta = \pi\sigma^3 n_0/6$. The wave-number integration is done with the mesh size $N = 300$ and the upper cutoff $\Lambda\sigma = 50$.

As can be seen from Eq. (2.11), our model for the dynamics of hard-sphere fluids depends on the packing fraction η and the metastability parameters y and κ. We recall that y describes the overall scale of the double-well potential for defects and κ is the appropriate ratio between the weak coupling and the low activation barrier as defined in Eq. (2.10). We first investigate whether the double-well potential and the coupling between the defects and the density fluctuations can be arranged to yield the slowing down of the dynamics. In order to see this, we solve Eq. (3.1) iteratively for given y, κ, and η. We find that for given packing fraction η, a nontrivial solution $f(q) > 0$ can be found and thus the dynamical slowing down is obtained for certain values of parameters y and

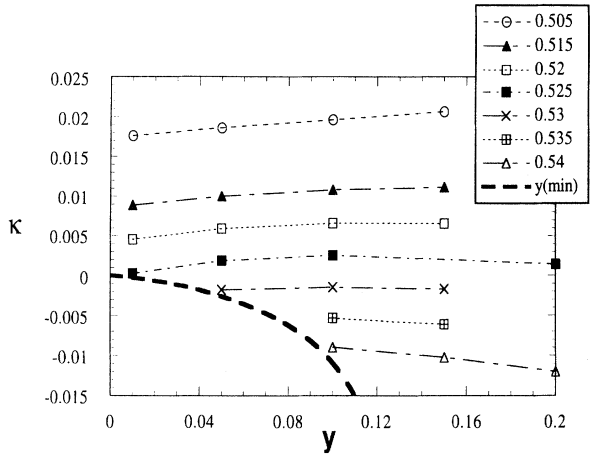

FIG. 1. The critical surface in the y-κ space for various values of packing fraction η. The thick dashed line is $y_{\min}(\eta)$. For $\eta \geq 0.53$, the critical surface does not extend to the small y ($y \leq y_{\min}$) regions.

κ. In fact, there exsists a critical surface in the y-κ space that separates the nonergodic [$f(q) > 0$] and the ergodic [$f(q) = 0$] phases. This critical surface can be found for various values of the packing fraction (see Fig. 1). This result is quite different from that found in the previous MCT studies of the hard-sphere system [7,19–21], which

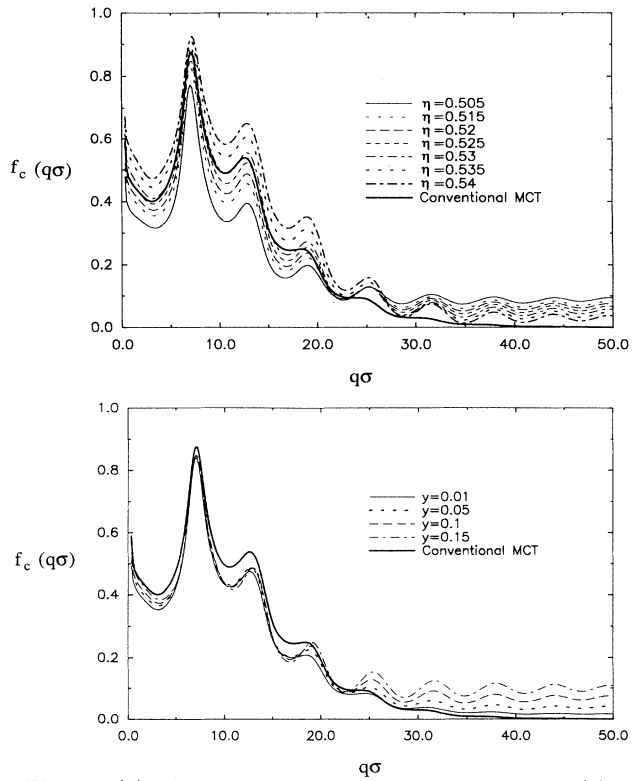

FIG. 2. (a) The critical nonergodicity parameter $f_c(q)$ for $y = 0.1$ and for various values of packing fraction (η). (b) The critical nonergodicity parameter $f_c(q)$ for packing fraction $\eta = 0.52$ and for various values of y. The thick solid line is $f_c(q)$ of the conventional MCT at $\eta = \eta_c \simeq 0.525$.

corresponds to the case where $y = \kappa = 0$. According to those studies, the transition occurs at the critical packing fraction $\eta_c \simeq 0.525$ [19]. This value is determined by the packing fraction at which the first nonvanishing solution of Eq. (3.1) appears when η is increased. The present analysis shows that the dynamical slowing down is controlled by the metastability parameters y and κ arranging themselves to be on the critical surface so that the transition occurs over a range of η which contains η_c of the conventional MCT.

For a given packing fraction, the values of κ on the critical surface do not change very much as shown in Fig. 1. As the packing fraction decreases, these critical values of κ increase. Since the hard-sphere system remains a fluid for a small enough packing fraction, the parameter κ should be bounded from above. The exact upper bound, however, is not determined in the present analysis for reasons discussed below. For high packing fractions $\eta \gtrsim 0.525$, the critical surface does not extend to the small y region: For $\eta \gtrsim 0.525$ and for y smaller than some value $y_{\min}$, one always has a nonvanishing solution $f(q)$ to Eq. (3.1). The value of $y_{\min}$ increases with increasing η (see Fig. 1). We note that for small packing fractions ($\eta \lesssim 0.505$) or for large y ($y \gtrsim 1.5$), the contribution to $f(q)$ from the large wave numbers become significant as seen in Figs. 2(a) and 2(b). This makes the present iteration analysis of Eq. (3.1) with the numerical large wave-number cutoff $\Lambda\sigma = 50$ less reliable for sufficiently small or large packing fractions. However, for the range of packing fractions, $0.51 \lesssim \eta \lesssim 0.54$, the present analysis clearly shows the slowing down of the dynamics.

For the parameters on the critical surface, one can determine the critical nonergodicity parameter $f_c(q)$ and the coefficient $h(q)$ as defined in Eqs. (3.5) and (3.7). In Figs. 2 and 3, $f_c(q)$ and $h(q)$ are shown for various values of η and y along with the corresponding quantities of the conventional MCT at $\eta = \eta_c$. In the framework of MCT, approaching the critical values of the parameters is represented by the parameter $\epsilon \to 0$ [see Eqs. (3.5) and (3.7)]. The conventional MCT analysis of hard-sphere fluids [7,19–21] is based on the assumption that the transition is actually controlled by the packing fraction approaching its critical value: $\epsilon \sim \eta - \eta_c$. Thus, in those analyses, the critical nonergodicity parameter $f_c(q)$ and the coefficient $h(q)$ are regarded as parameters independent of η. In the present model, however, the transition occurs when the system becomes metastable with the low

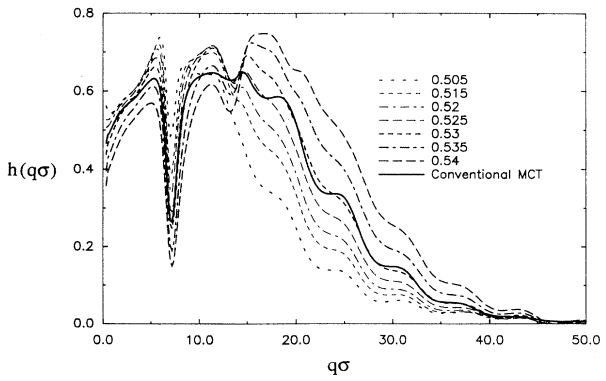

FIG. 3. The coefficient $h(q)$ describing the power-law and the von-Schweidler relaxations as expressed in Eqs. (3.5) and (3.7) for $y = 0.1$ and for various values of packing fraction (pf). The thick solid line is $h(q)$ of the conventional MCT at $\eta = \eta_c \simeq 0.525$.

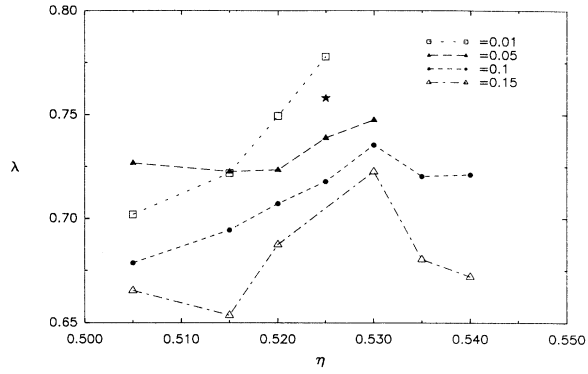

FIG. 4. The exponent parameter λ as a function of packing fraction η for various values of y. The star ($\star$) represents the conventional MCT value $\lambda \simeq 0.758$ at $\eta = \eta_c \simeq 0.525$.

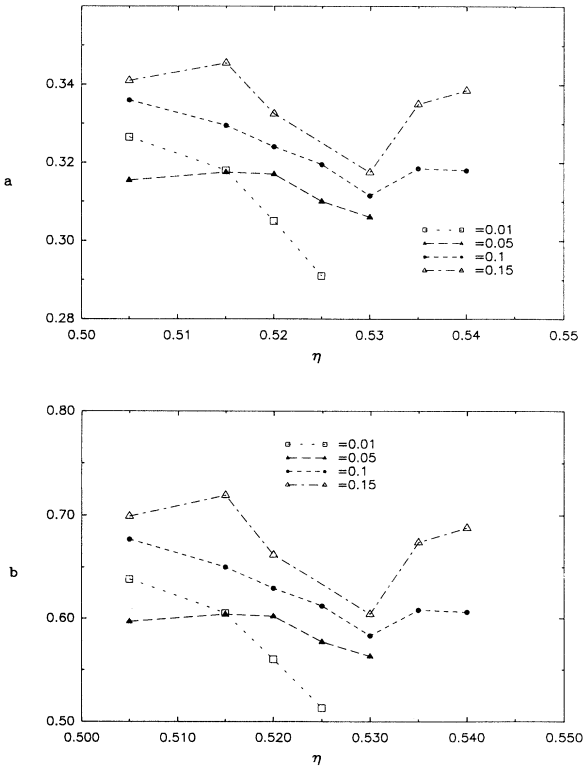

FIG. 5. The power-law and von-Schweidler exponents a and b as functions of packing fraction η for various values of y.

activation barrier ($\mu \to 0$) and the weak coupling ($x \to 0$) satisfying the condition $x/\mu^2 \to \kappa$ [see Eq. (2.10)], while the metastability parameters y and κ arrange themselves to be on the critical surface in y-κ space shown in Fig. 1. Thus, the control parameter in this case is proportional to μ. Therefore, in contrast to the conventional MCT, $f_c(q)$ and $h(q)$ depend on the parameter y describing the overall scale of the defect potential as well as the packing fraction. As one can see from Fig. 2 for fixed y, $f_c(q)$ shows a variation with η such that it has larger (smaller) values for low (high) wave numbers as the packing fraction increases.

For a given point on the critical surface, $(y, \kappa(y))$, one can calculate the exponent parameter λ using Eq. (3.2). Thus, in this model λ is determined as a function of η and y as shown in Fig. 4. Consequently, the exponents a and b characterizing the intermediate time regime are not subject to a particular value of packing fraction, instead they are given as smooth functions of η with one additional parameter y (see Fig. 5). As a function of the packing fraction, $\lambda(\eta)$ generally takes smaller values as one goes into the region of either small or large packing fractions. It should be noted in Fig. 4 that the values of λ become less reliable for large y ($y \gtrsim 1.5$) and small η ($\eta \lesssim 0.505$) because of the reason discussed above concerning the contribution from the large wave numbers. It is important to note that within the band of packing fractions $0.51 \lesssim \eta \lesssim 0.54$ where the dynamical slowing down is obtained, $\lambda(\eta)$ is not a constant as a function of η.

IV. DISCUSSION AND CONCLUSION

In this paper, we have been able to show how the metastability parameters describing the defects are incorporated in the structural arrest of hard-sphere fluids. The basic picture we obtain is that the transition is not a sharp one at a special value of packing fraction, but rather the transition occurs over a range of packing fractions as the metastability parameters arranging themselves to be on the critical surface as shown in Fig. 1.

In some sense, the present model just replaces the role played by the critical packing fraction $\eta_c \simeq 0.525$ of the conventional MCT of the hard-sphere system [7,19–21] in the slowing down of the dynamics by a band of packing fractions, $0.51 \lesssim \eta \lesssim 0.54$, which include η_c. However, our model has very different physical implications from the one studied in the conventional MCT in the following aspects. (1) In the conventional MCT, the exponent parameter λ is defined only at the critical packing fraction η_c, where its value is evaluated as $\lambda \simeq 0.758$ [20]. This value is somewhat larger than most of the values of λ found in the present model (see Fig. 4). Correspondingly, the values of the power-law and von-Schweidler exponents a and b in this model are larger than the conventional MCT values, $a = 0.301$ and $b = 0.545$. More importantly, since our model is not tied to the notion of η_c, the exponent parameter λ can be defined over a range of η. Furthermore, as a function of η, λ is not a constant. Instead, it shows a variation as shown in Fig. 4. (2) Other physical parameters such as the critical nonergodicity parameter $f_c(q)$ and the coefficient $h(q)$ describing the time relaxation sequence also depend on η in our model, while $f_c(q)$ and $h(q)$ are defined only at $\eta = \eta_c$ in the conventional MCT. These differences can be summarized in terms of the control parameter ϵ of each model such that in the conventional MCT, $\epsilon \sim \eta - \eta_c$ with the well-defined η_c and ϵ is proportional to the metastability parameter μ in the present model.

Recently, there have been many experiments on colloidal systems consisting of spherical particles [29–31], to which the MCT analysis of hard-sphere fluids has been applied. It is claimed in those experiments that the critical packing fraction η_c for the glass transition could be identified. The obtained values of η_c range from 0.555 to 0.575 for suspensions of PMMA particles [29,30] to 0.636 for microgels [31]. However, it is important to note that the identification of η_c in those experiments is carried out using somewhat indirect methods: For the PMMA system, η_c is taken as the value of η at which a homogeneously nucleated crystallization does not occur. For the system studied in Ref. [31], η_c is determined by fitting the experimental data against MCT results Eqs. (3.5) and (3.7) *assuming* that the control parameter is $\epsilon \sim \eta - \eta_c$. Thus, these experimental results should not be considered as conclusive evidence for the existence of η_c, which is defined by the packing fraction at which the density autocorrelation function $\phi(\mathbf{q}, t)$ shows a sharp ergodic-nonergodic transition, i.e., $\phi(\mathbf{q}, t)$ decays to a finite quantity if $\eta > \eta_c$ and to zero otherwise as $t \to \infty$. As we shall show below, one could instead find evidence from those experimental data that supports the basic picture described in this paper where the glass transition in the hard-sphere system is in fact not a sharp one at the well-defined transition density, but it results from the system becoming metastable.

As can be seen from the claimed values of η_c in those experiments, the values of packing fraction where the dynamical slowing down is observed are generally higher than the band of η, $0.51 \lesssim \eta \lesssim 0.54$ obtained here and also than $\eta_c \simeq 0.525$ of conventional MCT. This discrepancy has usually been neglected in the conventional MCT studies of the hard-sphere system [19–21]. In fact, in those analyses, only the difference $\eta - \eta_c$ is used to compare with the experimental data, where η_c of the conventional MCT is identified with the claimed values in the experiments. This discrepancy in η values between MCT and experiments is usually attributed [19] to the fact that MCT, without including the cutoff effect [10], tends to overestimate the tendency to freeze. We believe that this explanation also holds in the present case where η_c is replaced by the band of packing fractions. We note that the systems considered in those experiments do not have the ideal hard-sphere-type potential as their interparticle interactions, which might also contribute to this discrepancy.

In order to test experimentally the present picture of the dynamical slowing down in the hard-sphere system, one must study the dependence of the exponent parameter λ and the critical nonergodicity parameter $f_c(q)$ on the packing fraction η. A variation of these quantities as

a function of η would imply that the system undergoes a smooth transition without the special transition packing fraction. In the experiments mentioned above, λ and $f_c(q)$ are obtained by using Eqs. (3.5) and (3.7) to fit the intermediate time relaxation data of $\phi(\mathbf{q},t)$. But, unfortunately, in most cases [29,30], the analysis is carried out under the assumption that $\epsilon \sim \eta - \eta_c$. In particular, the value of λ is not obtained from the experimental data. Instead the conventional MCT value $\lambda \simeq 0.758$ is directly applied to the analysis of the data. Also the apparent variations of $f_c(q)$ with η observed in Refs. [29,30] are not systematically studied but neglected in the analysis. Thus, in order to see the η dependence of λ and $f_c(q)$, a more careful study of the experimental data is needed that treats λ, $f_c(q)$, $h(q)c_\epsilon$, and τ_a in Eqs. (3.5) and (3.7) as adjustable parameters without assuming any particular form for the control parameter ϵ.

In fact, this kind of analysis has been performed at one point of the discussion in Ref. [31]. For fixed wave number q, one can indeed see variations of λ and $f_c(q)$ values as functions of η (see Fig. 5 of Ref. [31]) when they are treated as free parameters. We note that the amount of variation of the exponent values is actually comparable to the present findings (see Figs. 4 and 5), although there are some differences between the actual values of the exponents a and b and the range of packing fractions over which the exponents are measured. The authors of Ref. [31] actually concluded that these variations are not systematic ones and treated λ and $f_c(q)$ as constants throughout their analysis. In order to see if these kind of data really show a dependence of the physical parameters, λ and $f_c(q)$ on η as described in the present analysis, which results from the metastable nature of the transition, a more detailed study is needed covering a wide range of values of the wave numbers and packing fractions.

The present model predicts that $f_c(q)$ and λ depend on η with one additional parameter y (see Figs. 2 and 4). We note that y is the dimensionless parameter which represents the overall scale of the potential energy for the defects. We interpret this metastability parameter y as something that depends on the microscopic details of the system and that may also have the packing fraction dependence in it, which is not, however, determined within the present theory. We believe that the parameter y could be specified in principle as a function of packing fraction through a comparison with more detailed experimental data showing the dependence of $f_c(q)$ and λ on η.

We emphasize that in this paper we are mainly concerned with the qualitative picture of the effect of the defect structure on the slowing down of the dynamics of the hard-sphere systems, since the defect structure has been approximated in a simple way using Eq. (2.5). Nevertheless, our model provides an important picture of smooth transition with the physical parameters such as the exponents a and b governing the time relaxation sequence and the critical nonergodicity parameter $f_c(q)$ depending smoothly on the packing fraction. And this general picture might be robust in more complex systems. An example of such system where the exponents depend smoothly on the temperature can be found in the experiment in Ref. [5].

We also note that we have focused on the intermediate time regime before the primary α relaxation. In this time regime, the defect autocorrelation function can be regarded as a constant in time [1,2] due to its long time scale. For the wave-number-independent case, one could extend the FNH formalism by considering the time dependence of the defect autocorrelation function as shown in Ref. [2]. One can in principle extend the present wave-number-dependent model to the primary relaxation regime by considering the full time and wave-number dependences of the density and the defect autocorrelation functions following Ref. [2]. The analysis of such a model, however, will be a very difficult task.

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