Mode-coupling effects on self-diffusion in a simple fluid at freezing

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The suppression of the self-diffusion constant D_L for a simple fluid in the long-time limit in comparison to the corresponding short-time or bare value is computed taking into account the mode-coupling effects to lowest order. We obtain a value of $D_L/D_0 = 0.11$ at the freezing density in close agreement with the observed value of 0.10 for different systems. [S1063-651X(96)03307-7]

I. INTRODUCTION

The single particle dynamics in a fluid is demonstrated through the behavior of the self-diffusion coefficient [1]. In a dense fluid, the motion of the single particle gets coupled to the hydrodynamic or collective modes in the fluid and this produces a suppression of the diffusion constant for a tagged particle. The ratio of the long-time self-diffusion constant D_L to its short or bare value D_0 was found to be close to 0.1 at freezing density for several liquids with different interaction potentials [2]. Subsequently Indrani and Ramaswamy [3] presented a fully self-consistent mode-coupling calculation to explain the fall in the value of the long-time diffusion constant. While this work constitutes an instructive way to explain the observed effect qualitatively, the formalism used by these authors is not proper as was pointed out by Fuchs [4] and also quantitatively not in agreement with the observed result. Mode-coupling theory [5,6] has been quite successfully used over the last few years to explain the dynamics of dense liquids approaching the onset of the glass transition. For supercooled liquids, a self-consistent form of the mode-coupling theory has been used. In these models the transport coefficients are expressed in terms of hydrodynamic correlation functions in a self-consistent manner. This produces a feedback to the transport processes from the slow decay of correlations in the system. While the self-consistent model has worked for the deep super cooled densities, for moderate densities it presents an over correction of the transport coefficients. The dynamics of the liquid at moderate densities can be described by the non-self-consistent (NSC) treatment of the mode-coupling effect. In this work, we adopt such an approach. The usefulness of this approach was discussed in detail in [7].

We consider the usual equations obtained for the mode-coupling kernels using fluctuating hydrodynamics [8,9] or microscopic methods [10] for the density correlation functions and the self-correlation functions. This is also in agreement with the comment of Ref. [4]. In computing the relaxation of the correlation, we use the correlation functions from bare theory—in other words, we treat the mode-coupling kernels in a non-self-consistent manner. Since the correlation functions accounted for the renormalization of the transport coefficients are taken from dynamical equations governed by the short-time or bare transport coefficients, in our approach one has to choose a model for short-time dynamics for a hard sphere system. The details of the model for

short-time dynamics of the density correlation was described in Ref. [7] and here we directly use the result from there for the calculation of the mode-coupling kernel. Using the NSC calculation, we obtain the value of D_L/D_0 to be 0.11. This is in close agreement with the recent results of Lowen, Palberg, and Simon [2].

In the next section, we briefly describe the model equations used. Section III describes the details of the calculation. We end the paper with a short discussion of the results.

II. DETAILS OF THE MODEL STUDIED

The theory is formulated primarily in terms of the dynamic correlation functions of collective density and the self- or tagged particle density. The normalized density-correlation function is given by

$$\psi(q,t) = \frac{\langle \delta\rho(q,t)\delta\rho(-q,t)\rangle}{\langle \delta\rho(q,0)\delta\rho(-q,0)\rangle}, \tag{1}$$

where the Laplace transform $\psi(q,z)$ of the density-correlation function defined as,

$$\psi(q,z) = -i \int_0^\infty dt\, e^{izt}\psi(q,t), \tag{2}$$

has a simple continued fraction representation involving the generalized transport coefficient $D(q,z)$

$$\psi(q,z) = \cfrac{1}{z - \cfrac{\Omega_q^2}{z + iD(q,z)}}, \tag{3}$$

with $\Omega_q^2 = q^2/[\beta m S(q)]$ as the microscopic frequency of the liquid state dynamics. Similarly, the self-correlation function or the Van Hove correlation function is obtained as

$$\phi^s(q,z) = \cfrac{1}{z - \cfrac{\Omega_{sq}^2}{z + i\Gamma^s(q,z)}}, \tag{4}$$

where $\Omega_{sq}^2 = q^2/(\beta m)$ and $\Gamma^s(q,z)$ are the appropriate memory functions for the self-correlation function. The

memory functions for the self- and density-correlation functions can be generally split into a short-time part and a long-time part,

$$D(q,z) = [\Gamma_0(q) + \Gamma_{mc}(q,z)], \qquad (5)$$

$$\Gamma^s(q,z) = [\Gamma_0^s(q) + \Gamma_{mc}^s(q,z)]. \qquad (6)$$

The short-time part in the memory functions refers to dynamics of the liquid over time scales in which the fluid particles undergo uncorrelated collisions. The second terms in Eqs. (5) and (6) describe the so called mode-coupling effects which become important over long-time scales accounting for correlated collisions. Explicit expressions for the mode-coupling terms can be obtained from theories of the liquid state and are given by [5,6,11,12]

$$\Gamma_{mc}(q,t) = \int \frac{d(\vec{k})}{(2\pi)^3 n*} V(q-k,k)\psi(|q-k|,t)\psi(k,t), \qquad (7)$$

where the mode-coupling vertex $V(q-k,k)$ is given by

$$V(q-k,k) = \frac{1}{\beta m}\left[\frac{(\vec{k})\cdot\hat{\vec{q}}nc(k) + \hat{\vec{q}}\cdot(\vec{q}-\vec{k})nc(|q-k|)}{q}\right]^2 \\ \times S(|q-k|)S(k),$$

with $c(k)$ being the direct correlation function for the liquid. Similarly, the memory function for the self-correlation function has the mode-coupling contribution,

$$\Gamma_{mc}^s(q,t) = \int \frac{d(\vec{k})}{(2\pi)^3 n*} V^s(q-k,k)\phi^s(|q-k|,t)\psi(k,t), \qquad (8)$$

where the corresponding mode-coupling vertex $V^s(q-k,k)$ is given by

$$V^s(q-k,k) = (\vec{k}\cdot\hat{\vec{q}})^2[nc(k)]^2 S(k). \qquad (9)$$

Equations (3) and (4) form a closed set of nonlinear integral equations for the density- and self-correlation functions. We inverse Laplace transform Eqs. (3) and (4) to write down the following second order differential equations in time for the density- and self-correlations, respectively.

$$\ddot{\psi}(x,t) + \Delta\left[g(x)\dot{\psi}(x,t) + x^2 S^{-1}(x)\psi(x,t) \right. \\ \left. + \int_0^t \Gamma_{mc}(x,t-\tau)\dot{\psi}(x,\tau)d\tau\right] = 0 \qquad (10)$$

and

$$\ddot{\phi}^s(x,t) + \Delta\left[\dot{\phi}^s(x,t) + x^2\phi^s(x,t) \right. \\ \left. + \int_0^t \Gamma_{mc}^s(x,t-\tau)\dot{\phi}^s(x,\tau)d\tau\right] = 0, \qquad (11)$$

with the wave vector expressed in the dimensionless form, $x = q\sigma$ and time t rescaled in terms of the unit of time τ_0. Δ and $g(x)$ are dimensionless quantities obtained as,

$$\Delta = \tau_0\Gamma_0^s, \quad g(x) = \Gamma_0/\Gamma_0^s. \qquad (12)$$

Here, we choose the time scale τ_0 in terms of the short-time or bare diffusion constant in the system as $\tau_0 = \sigma^2/D_0$.

Δ and $g(x)$ depend on the model used for the short-time dynamics of the system. In the present work we use the short-time-kinetic model [11] used for a simple hard sphere system. Equations (10) and (11) are solved using a linearized mode-coupling scheme in which the mode-coupling terms (7) and (8) are approximated by solutions of the corresponding linear equations for the correlation functions. At moderate densities, as is considered in the present work, this reproduces the correct relaxation times and will be used here for computing the mode-coupling effects on the self-diffusion coefficient.

III. NUMERICAL RESULTS

The long-time diffusion coefficient D_L can be obtained in terms of the memory function Γ_s^q being renormalized with the mode-coupling contribution. The ratio of D_L to D_0 is given by,

$$\frac{D_L}{D_0} = \frac{1}{1+\Sigma}, \qquad (13)$$

where Σ is now given by

$$\Sigma = \frac{2}{3}\int_0^\Lambda dx x^4 [1 - S(x)]^2 S(x)^{-1} \int_0^\infty dt\phi^s(x,t)\psi(x,t). \qquad (14)$$

For computing Σ from the above expression (14) the upper cutoff Λ of the wave vector integral is chosen to be equal to 25 which corresponds to a short enough length so that all the relevent structural effects are taken into account and for increasing the cutoff further does not produce much change in the calulated value of Σ. The cutoff in the time integral is extended to a long enough time scale to ensure convergence of the integral. The static structure factor $S(x)$ is approximated by the Percus-Yevick expression for a hard sphere system with a Verlet-Weiss correction. The mode-coupling contributions are computed using a non-self-consistent approach, i.e., the correlation functions in the mode-coupling kernels are solutions of linear equations.

In Fig. 1, we plot for the packing fraction given by $\eta = 0.47$, the decay of the density correlation function $\psi(q,t)$ (renormalized due to the mode-coupling effect) with time for the wave vector equal to the peak of the structure factor. The behavior for the correlation function without mode coupling is also shown by the dashed line. Figure 2 is similar to Fig. 1 but is for the self-correlation function. Using the renormalized correlation functions, we can estimate the integral given in (14) to get D_L/D_0 as a function of the density. In Table I we show the ratio of D_L/D_0 as obtained in the present work with the results [2] from the computer simulation of different systems. It is the universal value [3] of the peak of the static structure factor (≈ 2.85 that is cru-
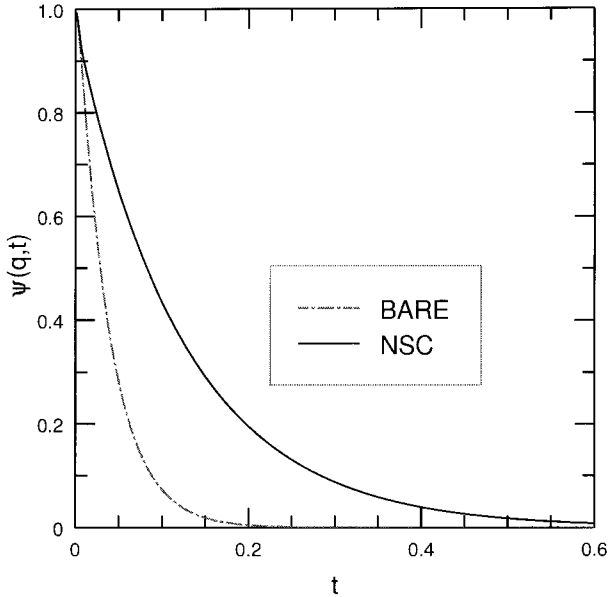
FIG. 1. Decay of the collective density correlations with time $t^* = t/\tau_0$ at a wave vector $q^* \equiv q\sigma$ corresponding to the structure factor peak. Solid line represents the data from the NSC calculation. Dashed line shows the decay without the mode-coupling effects.

FIG. 2. Decay of the self-correlations with time $t^* = t/\tau_0$ at a wave vector $q^* \equiv q\sigma$ corresponding to the peak of the structure factor. Solid line represents the data from the NSC calculation. Dashed line shows the decay without the mode-coupling effects.

cial in determining the mode-coupling contribution. If we use the static structure factor with and without the Verlet-Weiss correction the maximum of the structure factor peak reaches this value at packing fractions $\eta = 0.494$ and 0.470, respectively. Indeed the ratio D_L/D_0 in both the cases are equal to 0.11 showing the relevance of the value of $S(k)$ at the peak. The ratio of the long-time diffusion coefficient D_L to the short-time diffusion coefficient as predicted from a fully self-consistent theory is also shown in the table. At densities near freezing the fully self-consistent approximation produces an overestimation of the mode-coupling effect. As the packing fraction increases in the supercooled region beyond freezing densities a fully self-consistent calculation is necessary.

IV. DISCUSSION

We have considered here the mode-coupling contributions to the self-diffusion coefficient for a tagged particle and computed the ratio of the short-time or bare diffusion constant D_0 to the long-time diffusion constant D_L. Recent works [3] have considered this ratio using a fully self-consistent mode-coupling theory and report a value of 0.05. In a wide range of systems, D_L/D_0 was seen to be close to 0.1 at freezing. Moreover, the formalism used in [3] is not proper as was pointed out in a subsequent comment by
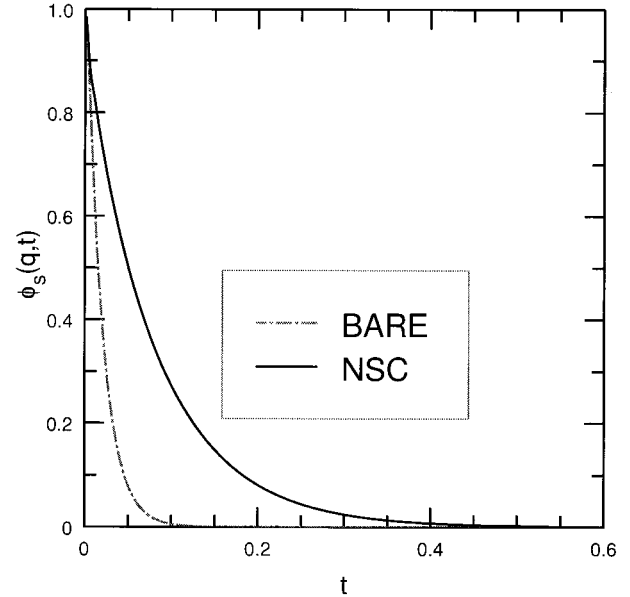
Fuchs. In the present work we consider the proper mode-coupling equations used in the literature for *dense* liquids. However, since the densities considered are near the freezing point we do not take a fully self-consistent approach as is done in theories of glass transition applicable to supercooled densities. A non-self-consistent calculation [7] at these densities also gives the right estimate for the viscosity of the liquid. Our method obtains a value of $D_L/D_0 \sim 0.11$, which is close to the observed value.

The mode-coupling contribution to the diffusion coefficient considered here signifies the effects coming from the coupling of the single particle density fluctuation with the hydrodynamic mode of collective density fluctuation in the fluid. This effect becomes enhanced at higher densities due to correlations building at successive collisions for a fluid particle, giving rise to the so called ring collisions in a kinetic description. This produces the slower power law decay of correlations in the fluid termed as long-time tails [13] for the transport coefficients as against a purely exponential decay of correlations. The latter is due to the uncorrelated random collisions of the fluid particles and is represented through the short-time or bare transport coefficients. In the present work we focus on the effect of this cooperative dynamics on the slowing of the long-time diffusion process in comparison to its short-time value. In computing the mode-coupling effects we have considered only the coupling of the

TABLE I. Comparison of D_L/D_0 at freezing, as obtained from theory and computer simulation.

System	Structure factor peak	D_L/D_0
One component plasma [2]	2.82	0.097
Hard sphere [2]	2.85	0.099
Self-consistent [4]	2.85	0.002
Non-self-consistent (present work)	2.85	0.107

self-density mode to the collective density fluctuations in the fluid. At freezing density this is the dominant coupling instead of the coupling between the self-diffusion modes [14]. However, the present result may be further improved by taking into account the effect of couplings of the other hydrodynamic modes in the theory at this order [15]. It is also useful to note that the cutoff mechanism [16,8] that eliminates the dynamic instability from self-consistent mode-coupling theories of glass transition is not crucial at the density we are considering in the present work. It is only at supercooled densities when the density fluctuations tend to cause a total structural arrest, the couplings to current fluctuations finally restores the ergodicity in the system eliminating a sharp transition to a nonergodic phase and all correlations finally decay over long enough time scales. In the present theory for densities near freezing point this is not very important.

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