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Power law mass dependence of diffusion: A mode coupling theory analysis

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The self-diffusion coefficient of a tagged molecule is known to exhibit a weak mass dependence, especially for solutes with size comparable to or larger than the size of the solvent molecules. Sometimes this mass dependence can be fitted to a power law, with a small exponent, less than 0.1. This weak mass dependence has often been considered as supportive of the hydrodynamic picture (that is, the Stokes-Einstein relation) of diffusion rather than the kinetic theory approach, which predicts a stronger mass dependence, for example, via the Enskog theory. Neither can explain the weak power-law mass dependence. In order to understand this, we have carried out a mode coupling theory (MCT) analysis of diffusion. It is found that a straightforward application of the existing mode coupling theory expressions lead to an inaccurate *mass dependence*—it predicts an increase of diffusion coefficient with an increase of the mass. We find that this is because of the inadequate description of the initial decay of the collective contributions to the friction. We have proposed a new prescription to accurately describe the short time dynamics of the density and the current term. In addition, we have modified the existing MCT by imposing the full self-consistency between the frequency-dependent friction and the mean square displacement over the whole time and frequency plane. Previously the self-consistency was performed only at the zero frequency level between the zero frequency friction and the diffusion coefficient. With these two generalizations, the mode coupling theory is found to provide a fairly accurate description of the mass dependence. In particular, the theory can correctly reproduce the power-law dependence of solvent-solute diffusion ratio on solute-solvent mass ratio, observed in computer simulations of Bearman and Jolly [Mol. Phys. **44**, 665 (1981)]. Another important result is that the current mode is found to play no significant role in determining the diffusion. Thus the hydrodynamic argument of weak mass dependence has little validity for same size solute-solvent systems.

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I. INTRODUCTION

The self-diffusion of a tagged solute molecule in a dense liquid is a subject of intense current discussion, which, given the long and illustrious history of the problem, is rather surprising. This current upsurge of interest, however, seems to be fuelled by the following factors. First, extensive computer simulations can now be carried out that allow one to ask and seek answers of detailed dynamic type. This was not possible before. Second, many recent experiments have been performed that seem to probe increasingly detailed aspects of dynamics of liquids. In order to understand the questions posed by the recent experiments, a much better understanding of diffusion is required. The study of diffusion can be used not only to understand the dynamics of the solvent but also to quantify the nature of the solute-solvent interactions. [1]. Third, the interactions involved in real systems are often much more complex than the simple Lennard-Jones type, which are usually assumed in theoretical and simulation studies. Thus, some of the studies have been directed to understand effects of specific solute-solvent interactions [2].

The diffusion of a solute is conventionally described by the well-known Stokes-Einstein (SE) relation,

$$D = k_B T / C \pi \eta R, \tag{1}$$

where D is the diffusion coefficient of the solute, R the radius, and η the viscosity of the solvent. The constant C is determined by the hydrodynamic boundary condition, being 4 for the slip and 6 for the stick boundary condition, respectively. As usual, $k_B T$ is the Boltzmann constant times the temperature. In the above relation, the influence of the dynamics of the solvent enters through the viscosity term while the effects of solute-solvent interactions are usually incorporated within the constant C and the radius R − the latter is often varied to fit the experimental data [3].

An important aspect of the Stokes-Einstein relation is that the predicted diffusion does not at all depend on the mass of the solute. This is completely opposite to the kinetic theory prediction. For example, the Enskog theory predicts a square root mass dependence, as given by the following expression:

$$D_E = \frac{3}{8 \rho \sigma^2 g(\sigma)} \sqrt{\frac{k_B T}{2 \pi \mu}}, \tag{2}$$

where μ is the reduced mass of the solute-solvent pair, σ is the diameter of the solvent, and $g(\sigma)$ is the value of the radial distribution function at contact. Equation. (2) predicts too strong a mass dependence that is not observed in computer simulation and experimental studies [4].

On the other hand, according to the SE relation the product $D\eta$ should remain constant for systems having particles of the same size and studied at the same temperature,

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whereas recent studies [5,6] have found that the SE relation does not hold when the mass of the particles are changed. Walser *et al.* have performed molecular dynamics (MD) simulations of water molecules with different mass and different molecular mass distribution [5]. They have shown that although the viscosity increases and the diffusion decreases with mass, the product of the two does not remain constant. The product $D\eta$ as they find is not correlated with the molecular mass, but it is correlated for those systems with the same mass distribution.

Thus neither the kinetic theory nor the hydrodynamic theory can predict the correct mass dependence of diffusion. Clearly, the hydrodynamic and the kinetic theories describe two opposite limits of diffusion. While the first one assumes the validity of the Navier-Stokes hydrodynamics at molecular length scales, the second one tends to describe diffusion only in terms of binary collisional dynamics. While hydrodynamics assumes that the diffusion occurs via the coupling of the solute velocity with only the collective transverse current mode of the solvent, the Enskog kinetic theory neglects coupling of the solute motion to all the hydrodynamic modes. In both these pictures the diffusion due to the structural relaxation of the surrounding solvent is totally neglected. The more recent mode coupling theory seems to interpolate between the two limits and takes into account the contributions of the structural relaxation.

Mode coupling theory has already been used to understand the effects of varying the solute-solvent size ratio $\mathcal{R}$ and also the effects of the specific solute-solvent interaction on the diffusion of a tagged solute molecule. It was found that a crossover from a structural relaxation dominated diffusion to the current mode dominated diffusion occurs as the solute size is increased [7]. This crossover was found to occur when the solute size was about twice as big as the solvent molecules. In a separate calculation, it was found that, in contrast to the hydrodynamic prediction, the nature of the solute-solvent interaction can alter the diffusion coefficient of the solute considerably [2]. This was explained in terms of the modification of the structure of the solvent surrounding the solute. The study showed that the diffusion coefficient decreases when the specific interaction is attractive but increases when this interaction is repulsive.

In this paper we extend the mode coupling theory calculation to study the mass dependence of tagged molecule diffusion. Here, however, the situation turned out to be quite different. When the solute mass becomes significantly larger than the solvent molecules, the expression for the density contribution to friction (as used by Sjogren and Sjolander [8] and also by Balucani and Zoppi [9]) leads to an inaccurate result – *it predicts an increase of diffusion with mass*. The reason is that the short time descriptions of both the density and the current mode contributions to the friction were at fault. This needed to be rectified within the mode coupling formalism. We show here that the proper way to implement the separation of time scales between the binary dynamics and the collective dynamics is to properly remove the short time dynamics from the collective part. This is achieved by considering that the short time dynamics of the collective part is represented by the free inertial motion of the solute and the short time collective dynamics of the solvent and not the full solvent dynamics.

In addition, we have introduced an alternative method to calculate the frequency-dependent friction self-consistently with the mean square displacement. The self-consistency is now imposed *over the whole time and frequency plane*. In the existing works [7,2] the self-consistency was imposed only on the zero frequency friction.

The modified theory is found to provide an accurate description of the dependence of the diffusion coefficient of the solute on mass. We find a power-law mass dependence of the diffusion that is in good agreement with the simulation results of Bearman and Jolly [1]. The value of the exponent we find is equal to 0.099. The reason for the weak power-law dependence is that the mass dependence enters largely through the binary term whose contribution is small in dense liquids. In addition, the contribution of the density term moves in the opposite direction when the mass is increased, thus further weakening the effects of the binary term.

The organization of the rest of the paper is the following. Section II A deals with the theoretical formulation where we propose a modification in the existing theory; Sec. II B provides a graphical analysis of how and where the existing theory was going wrong in describing the short time dynamics of the collective parts and also justifies the new proposed modification. Section III contains the numerical results and Sec. IV concludes with a brief discussion.

II. THEORY OF DIFFUSION

A. Extensions of the mode coupling formalism

We present here the modified expressions of the mode coupling theory used in the present work.

The system studied in this paper consists of one solute molecule of mass M and the N solvent molecules, each of mass m. The pair potential of the solvent-solvent pair and the solute-solvent pair is assumed to be given by the simple Lennard-Jones 12-6 potential

$$v(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{3}$$

where ϵ is the energy scale of the pairwise solvent-solvent interaction, σ is the diameter of both the solute and the solvent, and r is the distance between two molecules. The system is characterized by two dimensionless parameters, reduced density $\rho^*=\rho\sigma^3$ and reduced temperature $T^*=k_BT/\epsilon$.

The microscopic expression of the friction is given by the following equation [8]:

$$\zeta(z)=\frac{1}{k_BTmV}\int d1,\ldots,d2'[\hat{\mathbf{q}}\cdot\nabla_{\mathbf{r}_1}v(\mathbf{r}_1-\mathbf{r}_2)]G^s(12;1'2',z)[\hat{\mathbf{q}}\cdot\nabla_{\mathbf{r}_1'}v(\mathbf{r}_1'-\mathbf{r}_2')], \tag{4}$$

where the four-point function $G^s(12;1'2',t')$ describes the correlated motion of the solute and the solvent particles. It describes the time dependent probability that the solute moves from the position (r_1',p_1') at t' to position (r_1,p_1) at t and a solvent particle that is located at (r_2',p_2') at t' and the same or some other solvent particle is found at (r_2,p_2). $G^s(12;1'2',t')$ also contains information on the static correlation between the tagged particle and the solvent particles through its initial value $\tilde{G}^s(12;1'2')$. z is the Laplace frequency.

The mode coupling expression for the frequency-dependent friction is given by [7,8]

$$\frac{1}{\zeta(z)}=\frac{1}{\zeta_D(z)+R_{\rho\rho}(z)}+R_{TT}(z), \tag{5}$$

where $\zeta_D(t)$ is the binary part of the friction, $R_{\rho\rho}(t)$ is the friction due to the coupling of the solute motion to the collective density mode of the solvent, and $R_{TT}(t)$ is the contribution to the diffusion (inverse of friction) from the current modes of the solvent. In writing Eq. (5), we have neglected the longitudinal current term, which makes a small contribution at the densities considered in this paper [7,8].

The expression of the binary friction $\zeta_D(t)$, for different solute-solvent mass ratio, is given by

$$\zeta_D(t)=\omega_{o12}^2\exp(-t^2/\tau_\zeta^2), \tag{6}$$

where ω_{o12} is now the Einstein frequency of the solute in presence of the solvent and is given by

$$\omega_{o12}^2=\frac{\rho}{3M}\int d\mathbf{r}g(r)\nabla^2 v(r). \tag{7}$$

Here $g(r)$ is the radial distribution function.

In Eq. (6), the relaxation time τ_ζ is determined from the second derivative of $\zeta_D(t)$ at $t=0$ and is given by

$$\omega_{o12}^2/\tau_\zeta^2=(\rho/6M\mu)\int d\mathbf{r}[\nabla^\alpha\nabla^\beta v(\mathbf{r})]g(\mathbf{r})[\nabla^\alpha\nabla^\beta v(\mathbf{r})] \\ +(1/6\rho)\int[d\mathbf{q}/(2\pi)^3]\gamma_d^{\alpha\beta}(\mathbf{q})[S(q)-1]\gamma_d^{\alpha\beta}(\mathbf{q}), \tag{8}$$

where summation over repeated indices is implied. μ is the reduced mass of the solute-solvent pair. Here $S(q)$ is the static structure factor. The expression for $\gamma_d^{\alpha\beta}(\mathbf{q})$ is written as a combination of the distinct parts of the second moments of the longitudinal and transverse current correlation functions $\gamma_d^l(\mathbf{q})$ and $\gamma_d^t(\mathbf{q})$, respectively,

$$\gamma_d^{\alpha\beta}(\mathbf{q})=-(\rho/M)\int d\mathbf{r}\exp(-i\mathbf{q}\cdot\mathbf{r})g(\mathbf{r})\nabla^\alpha\nabla^\beta v(\mathbf{r}) \\ =\hat{q}^\alpha\hat{q}^\beta\gamma_d^l(\mathbf{q})+(\delta_{\alpha\beta}-\hat{q}^\alpha\hat{q}^\beta)\gamma_d^t(\mathbf{q}), \tag{9}$$

where $\gamma_d^l(\mathbf{q})=\gamma_d^{zz}(\mathbf{q})$ and $\gamma_d^t(\mathbf{q})=\gamma_d^{xx}(\mathbf{q})$.

Note that in Eq. (7) if the solute and the solvent mass are both assumed to be *m*, we recover the expression of the binary time scale derived by Sjogren and Sjolander for neat liquids [8]. Thus the modification does not change the expression of the binary part of the friction or its time scale.

We modify the existing expression for the density mode coupling term in the following way. We assume that the binary part of the friction includes that part, which *only* contributes to the rapid renormalization of the medium due to a binary collision. This means that we need to remove from the density and the current terms not only the short time motion of the solute but also that of the solvent. With this assumption, the expression for $R_{\rho\rho}(t)$ for different solute-solvent mass ratio can be written as

$$R_{\rho\rho}(t)=\frac{\rho k_BT}{M}\int[d\mathbf{q}'/(2\pi)^3] \\ \times(\hat{q}\cdot\hat{q}')^2q'^2[c(q')]^2[F^s(q',t)F(q',t) \\ -F_o^s(q',t)F_o(q',t)], \tag{10}$$

where $F_0^s(q,t)$ and $F_0(q,t)$ denote the inertial limits of the self-intermediate scattering function of the tagged molecule and the intermediate scattering function of the solvent, respectively.

Similarly the expression for $R_{TT}(t)$ is given by

$$R_{TT}(t)=\frac{1}{\rho}\int[d\mathbf{q}'/(2\pi)^3][1-(\hat{q}\cdot\hat{q}')^2] \\ \times[\gamma_{d12}^t(q')]^2\omega_{o12}^{-4}[F^s(q',t)C_{tt}(q',t) \\ -F_o(q',t)C_{tto}(q',t)]. \tag{11}$$

Note that in the expression of $R_{\rho\rho}(t)$ and $R_{TT}(t)$, the short time part is now the product of the inertial motion of the solute and the short time collective dynamics of the solvent, instead of the full dynamics of the solvent.

Equations. (10) and (11) are presented here as alternative solutions. Several other prescriptions for subtracting the short time dynamics have been used in the past [8–11]. While we have not analyzed all of them in detail, the prescriptions used by Sjogren and Sjolander [8], by Balucani and Zoppi [9] and also by us earlier [7], lead to an inaccurate mass dependence of the self-diffusion coefficient, as discussed in the Introduction.

In Eqs. (10) and (11), $c(q)$ is the two-particle direct correlation in the wave number (q) space that is obtained from the HMSA scheme [12], which has also been used to obtain the radial distribution functions required to calculate the binary time constant and the vertex functions. $F(q,t)$ is the intermediate scattering factor and $C_{tt}(q,t)$ is the current autocorrelation function of the solvent. The expression and the calculation details of the above mentioned dynamical variables are given elsewhere [7]. Since both are pure solvent properties the mass that enters in the calculation is the solvent mass.

The other solvent dynamical variables required to calculate the density and current mode contributions are the inertial part of the intermediate scattering function $F_o(q,t)$ given by

$$F_o(q,t)=S(q)\exp\left(-\frac{q^2t^2}{2mS(q)}\right) \tag{12}$$

and the inertial part of the the current autocorrelation function $C_{tto}(q,t)$ given by

$$C_{tto}(q,t)=\frac{k_BT}{m}\exp\left(-\frac{\omega_t^2(q)t^2}{2}\right), \tag{13}$$

where $\omega_t^2(q)$ is the second moment of the transverse current correlation function [7,8].

The solute dynamical variables required to calculate the density and current contribution are the inertial part of the self-intermediate structure factor $F_o^s(q,t)$ given by

$$F_o^s(q,t)=\exp\left(-\frac{k_BT}{M}\frac{q^2t^2}{2}\right) \tag{14}$$

and the self-intermediate structure factor $F^s(q,t)$. Assuming Gaussian approximation the expression for $F^s(q,t)$ can be written as

$$F^s(q,t)=\exp\left(-\frac{q^2\langle\Delta r^2(t)\rangle}{6}\right), \tag{15}$$

where $\langle\Delta r^2(t)\rangle$ is the mean square displacement (MSD) that can be obtained from the time dependent velocity autocorrelation function (VACF), $C_v(t)$, through the following expression:

$$\langle\Delta r^2(t)\rangle=2\int_0^t d\tau C_v(\tau)(t-\tau). \tag{16}$$

The time dependent VACF is obtained by numerically Laplace inverting the frequency-dependent velocity autocorrelation function, which is related to the frequency-dependent friction through the following generalized Einstein relation:

$$C_v(z)=\frac{k_BT}{M[z+\zeta(z)]}. \tag{17}$$

Thus in this scheme the frequency-dependent friction has been calculated self-consistently with the MSD.

The self-consistency is implemented through the following iterative scheme. First, the VACF is obtained from Eq. (17) by replacing the total frequency-dependent friction $\zeta(z)$ by its binary part $\zeta_D(z)$. The VACF thus obtained is used to calculate the MSD through Eq. (16). Now this MSD is used to calculate $R_{\rho\rho}(t)$ and $R_{TT}(t)$ and thus $\zeta(z)$. This total friction is used to calculate the next VACF, which again is used to determine MSD and thus $\zeta(z)$. This iterative process is continued until the VACF obtained from two consecutive steps overlap.

Once the VACF is obtained self-consistently, the diffusion coefficient D is calculated using the following relation between the diffusion coefficient and the time dependent velocity autocorrelation function,

$$D=\tfrac{1}{3}\int_0^\infty d\tau C_v(\tau). \tag{18}$$

Note that in the above expressions, the mass of the solute enters in a complex fashion. First, it enters in the binary friction—even here the contribution is more complex than what was envisaged in the Enskog theory. The mass also enters in the collective contributions.

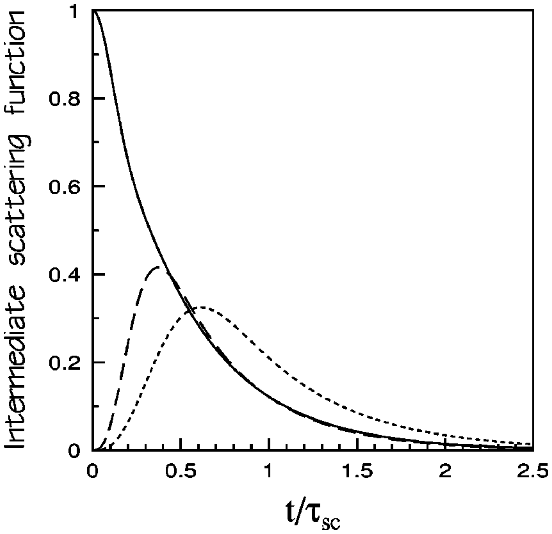

FIG. 1. The normalized intermediate scattering function of the solvent and the self-intermediate scattering functions (taking out the inertial part) of the solute for two different solute-solvent mass ratios are plotted against reduced time. The solid line represents the intermediate scattering function of the solvent, the long dashed line represents the self-intermediate scattering function of the solute for $M/m=1.0$ and the short dashed line represents the same for $M/m=3.0$. The plots are at $\rho^*=0.844$ and $T^*=0.728$. The time is scaled by $\tau_{sc}=\sqrt{m\sigma^2/k_BT}$.

B. Proper description of the short time dynamics in the collective mode contributions

As discussed in Sec. II A the standard prescription of the short time dynamics of the collective modes is erroneous. Although for the same mass, the absolute value of the friction is not affected, this error becomes transparent when the mass of the solute is significantly larger than that of the solvent molecules.

In order to have a pictorial understanding of the time scale argument presented we do the following analysis. Let us recall that in the mode coupling theory formalism, one needs to subtract the binary contribution from the collective terms. This is because at very short times (when terms of the order t^2 are only important), only the binary term is relevant. According to the existing prescriptions, this can be achieved by subtracting the free inertial motion from the self-dynamic structure term, that is, instead of $F^s(k,t)$, we should have $F^s(k,t)-F_o^s(k,t)$ multiplying the rest of the integrand, both in the density and in the current mode contributions. The time scale in the binary part given by Eq. (8) is determined by both the mass of the solute and the solvent and since effective mass enters the calculation it is mostly the mass of the lighter particle that determines τ_ζ. On the other hand, the time scale of the decay of $F_o^s(k,t)$ is determined only by the mass of the solute. When the mass of the solute becomes very large then the time scale of $F_o^s(k,t)$ becomes much larger compared to that of the binary time scale.

That the existing MCT decomposition indeed leads to a serious problem is shown in Fig. 1, where we compare $F^s(k,t)-F_o^s(k,t)$ with the dynamic structure factor $F(k,t)$, as a function of time for different mass ratios. It can be seen from this figure that for massive solutes, diffusion is coupled to solvent dynamics *only* at longer times, which is clearly

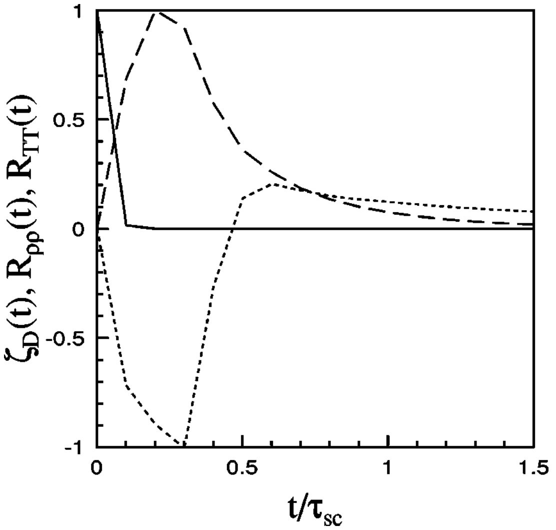

FIG. 2. The normalized contribution from the binary collision and the density term to the friction and the current term to the diffusion are plotted against reduced time. The solid line represents the time dependent binary term $[\zeta_D(t)]$, the long dashed line the time dependent density term $[R_{\rho\rho}(t)]$, and the short dashed line the time dependent current term $[R_{TT}(t)]$. The plots are at $\rho^*=0.844$ and $T^*=0.728$. The time is scaled by $\tau_{sc}=\sqrt{m\sigma^2/k_BT}$. The friction is scaled by τ_{sc}^{-1}.

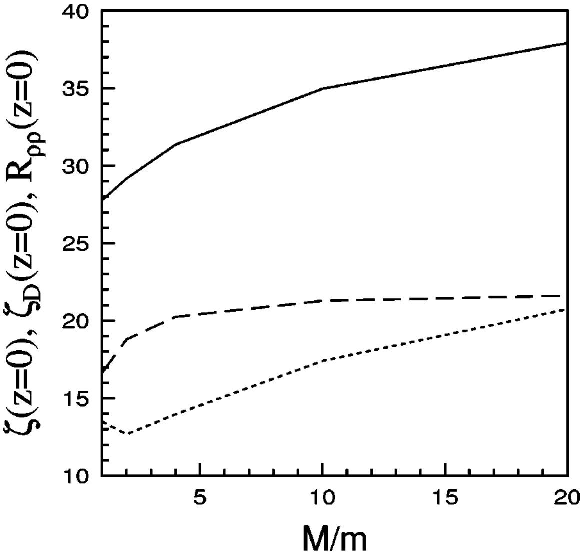

FIG. 3. The total friction (represented by solid line), the binary contribution to the friction (represented by long dashed line), and the density contribution to the friction (represented by the short dashed line) are plotted against the solute-solvent mass ratio at $\rho^*=0.844$ and $T^*=0.728$. The friction is scaled by τ_{sc}^{-1}.

unrealistic. According to our definition, the short time dynamics of the collective part is now given by the product of the inertial part of the solute dynamics to the inertial part of the solvent dynamics and not to the full solvent dynamics. Thus the time scale of decay of the short time dynamics in the collective parts that is $F_o^s(q,t)F_o(q,t)$ and $F_o^s(q,t)C_{tto}(q,t)$ will be determined by both the mass of the solute and the solvent and mostly by the mass of the lighter particle as in the case of the binary term.

III. RESULTS

With the above mentioned modifications properly defining the short time dynamics of the collective terms and also incorporating the self-consistency between the frequency-dependent friction and the mean square displacement over the whole frequency and time plane, we have calculated the mass dependence of the solute diffusion at $\rho^\star=0.844$ and $T^\star=0.728$.

According to mode coupling theory formalism, the binary term is expected to make a contribution in the short time. The density term that renormalizes the binary friction is expected to contribute in the intermediate time regime and the current term in the long time regime. Thus the three different terms in the expression of the friction/diffusion have different time scales. This is demonstrated in Fig. 2 by plotting the normalized (the maximum of the respective terms) time dependent contribution from the binary and the density term to the friction and the contribution from the current term to the diffusion, for solute-solvent mass ratio 1. The oscillation present in the current mode contribution is due to the oscillation in the current autocorrelation function. The long time tail in the current mode contribution becomes more prominent at lower density and higher temperature. The binary collision time is found to be 126 fs.

Note that Fig. 2 has been plotted with normalized functions in order to emphasize the time scales. The absolute value of the zero time friction is quite large. For example, for neat liquid, it is equal to 358.2 (in the unit of τ_{sc}^{-2}) at the density $\rho^*=0.85$ and $T^*=0.73$. The maximum value of the density term is about 10% of this value (near 40) while that of the transverse current term is only about 3% of the zero time friction value. The contribution of the longitudinal current term is much less and is not shown in the figure. The above numbers of course change when the mass of the solute is changed, but the contribution of the transverse current term increases slightly with mass.

The main result of this work is that the self-diffusion coefficient of the solute is found to have a weak mass dependence. The diffusion is found to decrease as the mass of the solute is increased. In Fig. 3, we have plotted both the binary and density term contribution to the total zero frequency friction against the mass ratio. We find that the current term contribution remains small and almost unaltered over the whole range of solute-solvent mass ratio studied in this article.

The same plot also shows that the binary part of the friction increases slowly and monotonically with the solute mass. On the other hand, the density term is first found to decrease for solutes almost twice as massive as the solvent and then it increases with the mass of the solute. The reason behind this initial decrease of the density term with the mass of the solute is the following. The maximum contribution from the density term to the total friction occurs around $q\sigma=2\pi$. Now the time scale of the short time collective motion of the solvent $F_o(q,t)$ is larger than the time scale of the inertial motion of the solute of the same mass at this wave number. As we increase the mass of the solute, the time scale of its inertial motion increases and thus $F_o(q,t)F_o^s(q,t)$ increases till the time scale of the inertial motion of the solute becomes larger than the time scale of the short time collec-

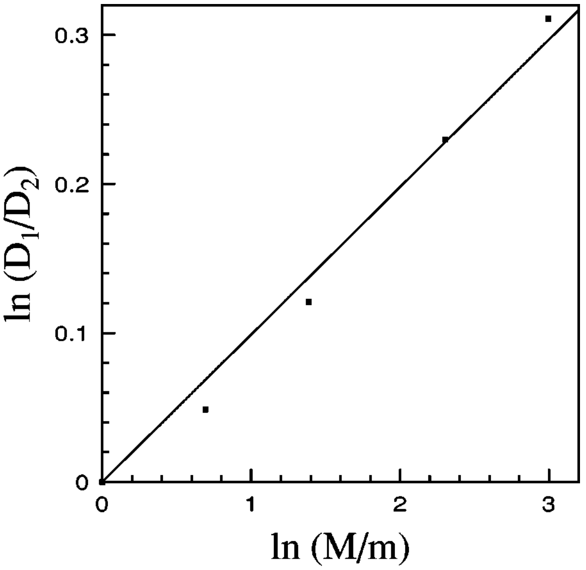

FIG. 4. $\ln_e D_1/D_2$ vs $\ln_e M/m$ is plotted at $\rho^*=0.844$ and $T^*=0.728$, where D_1 is the self-diffusion of the solvent, and D_2 that of the solute. M and m are the masses of the solute and the solvent, respectively. The slope of the straight line is 0.099. The plot shows a power-law mass dependence of the solute diffusion. The slope of the plot suggests that this mass dependence is weak.

tive dynamics of the solvent. We find that till the solute-solvent mass ratio is below 2, the inertial time scale of the solute remains smaller and $F_o(q,t)F_o^s(q,t)$ increases with the mass of the solute. Now the increase in the product $F_o(q,t)F_o^s(q,t)$ decreases the contribution from the density term. Thus we find that the contribution from the density term initially decreases with the solute-solvent mass ratio and then increases with it. Though the density term decreases initially we find that the total friction always increases with the mass of the solute. The initial increase being a little slower due to the opposite effect of the solute mass on the density and the binary term.

The most interesting result obtained from this study is the power-law dependence of the solute diffusion on mass as has also been observed in computer simulation studies [1]. The power-law dependence is clearly manifested in Fig. 4 where we have plotted $\ln D_1/D_2$ against $\ln M/m$, where D_1 is the diffusion of the solvent and D_2 is the diffusion of the solute. The slope of the line is 0.099. This implies a weak mass dependence of the solute diffusion, in agreement with the MD simulation results.

IV. CONCLUSION

Let us first summarize the main results of this paper. We show that the existing MCT prescription leads to inaccurate results, showing an increase in the diffusion value as the mass of the solute is increased. We traced back this problem to the erroneous description of the short time dynamics in the density and current mode contribution to the total friction. We show that according to the existing theory although the time scale of decay of the binary term is determined by both mass of the solute and the solvent, the time scale of the short time dynamics of the collective terms were given by the free solute motion and the full dynamics of the solvent. For massive solutes this leads to coupling of the solute dynamics to the density and current of the solvent *only* at longer time, which is clearly unrealistic. We have proposed a modification of the existing MCT where now the short time dynamics of collective term is given by the free inertial motion of the solute and the short time collective motion of the solvent. Thus the time scale of the short time dynamics of the collective part is now determined by either the time scale of the free inertial motion of the solute or the time scale of the collective short time dynamics of the solvent, whichever being smaller. This is in accord with the binary time scale. We have also introduced a self-consistent way of calculating the frequency-dependent friction with the mean square displacement. The self-consistency introduced in the previous works were only between the zero frequency friction and the diffusion coefficient. This alternative method takes care of introducing the self-consistency over the whole time and frequency plane.

After modifying the existing MCT we have calculated the mass dependence of the solute diffusion. The solute diffusion shows a weak mass dependence. We find a power-law dependence of the solute diffusion on mass that is in accord with the existing computer simulation results [1].

What is the origin of the weak power-law dependence of diffusion on the mass? This dependence comes mostly from the binary, that is, short time dynamics. Since the contribution of the binary term to the total friction is about 30–40 % in the liquid, the dependence on mass is naturally weaker than the prediction of the kinetic theory. Another important factor is that the density term first decreases with the increase of mass, although it increases later. Thus, for small changes of mass (a factor of 2 or so), the increase of friction from the binary term will partly be cancelled by the decrease from the density term. However, the negligibly small contribution from the current implies that the hydrodynamic logic of weak mass dependence is not valid.

The predictions from the mode coupling theory could be tested against molecular dynamics simulations. The modifications of the mode coupling theory proposed here should be useful in the study of other problems. Another important problem in this area is the much stronger mass dependence of the viscosity, observed in simulations [5]. The same effect is observed between ordinary and heavy water whose understanding is still awaited. As the difference between water and heavy water can at least partly be modelled by using a different interaction energy parameter ϵ, one can attribute this anomaly partly to the dynamics and partly to the statics. We hope to address these problems in future.

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