

Anomalous diffusion of small particles in dense liquids

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We present here a microscopic and self-consistent calculation of the self-diffusion coefficient of a small tagged particle in a dense liquid of much larger particles. In this calculation the solute motion is coupled to both the collective density fluctuation and the transverse current mode of the liquid. The theoretical results are found to be in good agreement with the known computer simulation studies for a wide range of solute–solvent size ratio. In addition, the theory can explain the anomalous enhancement of the self-diffusion over the Stokes–Einstein value for small solutes, for the first time. Further, we find that for large solutes the crossover to Stokes–Einstein behavior occurs only when the solute is 2–3 times bigger than the solvent molecules. The applicability of the present approach to the study of self-diffusion in supercooled liquids is discussed. © 1997 American Institute of Physics. [S0021-9606(97)51805-8]

I. INTRODUCTION

Diffusion of small solute particles (atoms, molecules) in a dense liquid of larger particles is an important but ill-understood problem of condensed matter physics and chemistry. In this case one does not expect the Stokes–Einstein (SE) relation between the diffusion coefficient (D) of the tagged particle of radius (R) and the viscosity (η) of the medium to be valid. Indeed, experiments^{1,2} have repeatedly shown that in this limit the SE relation significantly *underestimates* the diffusion coefficient. The conventional SE relation is $D = Ck_B T / R\eta$, where $k_B T$ is the Boltzmann constant times the absolute temperature and C is a numerical constant determined by the hydrodynamic boundary condition. To explain the enhanced diffusion, sometimes an empirical modification of the SE relation of the form $D = \text{const}/\eta^\alpha$ is used,¹ where the value of the exponent is typically $\alpha \approx 2/3$. The fractional viscosity dependence of D is often referred to as the microviscosity effect. On the other hand, Zwanzig and Harrison³ proposed that it is more meaningful to discuss the experimental results in terms of an *effective* hydrodynamic radius which is determined, among many factors, by the solute–solvent size ratio. Neither the fractional viscosity dependence of D nor the origin of the effective hydrodynamic radius are well understood. Another unresolved problem is a quantitative understanding of the crossover to SE behavior, which is expected as the solute size is increased far beyond that of the solvent.

Note that the above problems are unsolved even for dense liquids in the normal temperature–pressure conditions. When the liquid is supercooled below its freezing point, several additional (and interesting) anomalies are known to appear which are the subject of intense research at present.⁴ The present work is, however, limited to normal liquids only.

Although detailed microscopic calculations of the problems mentioned above are not available, there exist several

computer simulation studies,^{5,6} particularly for small solutes, which also find the anomalous enhanced diffusion, even for simple model potentials such as the Lennard-Jones. The physical origin of the enhanced diffusion is not clear from the simulations. We present here a microscopic calculation of the size dependent diffusion based on the recently developed mode coupling theory. The theory gives excellent agreement with the simulation results and provides a physical interpretation of the enhanced diffusion. In addition, a study of the crossover to the SE behavior at large solute sizes is presented. The expression of the friction used in this study is a well-known mode coupling expression. But in our case, as we have studied friction on a solute which is different in size from the solvent, we had to extend the mode coupling expression of friction for a pure system to that for a binary system.

The layout of the rest of the paper is as follows. Section II deals with the theoretical formulation. Section III contains the numerical results and comparison with experiments. Finally, Sec. IV concludes with a brief discussion on the results. Mathematical details are present in the Appendix.

II. THEORETICAL FORMULATION

Let us consider a single tagged solute particle among the solvent molecules. Let $v_{12}(r)$ denote the interaction pair potential between the solute and a solvent molecule, while $v(r)$ denotes the same for a pair of solvent molecules. Both are assumed to be given by the Lennard–Jones potential and are characterized by the same energy parameter. The other relevant interaction parameter, the LJ diameter, is denoted by σ_1 and σ_2 for the solvent and the solute, respectively. $\mathcal{R}^{-1} = \sigma_2/\sigma_1$ is the solute-to-solvent size ratio. The liquid is characterized by its number density ρ and absolute temperature T . We shall use the reduced density $\rho^* = \rho\sigma_1^3$ as a measure of the density of the liquid and shall concentrate on the high density limit for which detailed computer simulation results are available.

At a purely microscopic level the motion of a tagged particle in a dense liquid can be described in terms of an

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inertial motion of the particle, interrupted by rather hard repulsive collisions with the surrounding solvent particles. The inertial motion is not free; it occurs in the force field of the neighboring molecules. The difficulty describing this motion comes from the structure of the liquid which is isotropic on the long length scale but which exhibits pronounced short range order. Thus, the collisions are strongly correlated. The short time direct collision between the tagged particle and the solvent molecules can be described within certain approximation via the Enskog binary collision expression. The other is a long time process which is the correlated recollision of the tagged particle with the same solvent molecules. The correlated collision takes place due to the coupling of the solute motion with the different hydrodynamic modes of the solvent. The hydrodynamic modes which have been found to make contribution to the diffusive motion of the tagged particle are the density fluctuation and the transverse current mode. The neighboring solvent molecules create a cagelike structure around the tagged particle which hinders the motion of the particle. The density fluctuation causes the structural relaxation of the solvent, which is actually the relaxation of this cage. The slower the structural relaxation, the less the tagged particle can migrate. Coupling to the transverse current mode helps the particle to diffuse with the aid of the natural current of the solvent. The strength of the coupling of the solute motion to these two hydrodynamic modes depends on the density of the solvent and also on the solute-to-solvent size ratio. Theoretical studies have revealed the following picture: At low density and for a comparable solute-solvent size ratio, it is the direct collision part which dominates the friction, as here both the solvent cage and the flow of the natural current of the solvent are not fully developed. At intermediate density, it is the current mode which makes a major contribution to the friction as the solvent cage relaxes very fast in this density regime. The situation changes drastically at high density and in supercooled liquids where the density relaxation becomes very slow. Here, the primary contribution to the friction, and hence the diffusion, comes from the coupling of the solute's velocity field to the solvent density fluctuations. However, even here the picture may be quite different for very large and also for very small solutes. When the solute is larger than the solvent particle, then the caging effect of the solvent particles on the solute is not pronounced as the solute cannot probe the microscopic structure of the solvent. It is mainly the natural current of the solvent that then determines the motion of the solute. Again, when the solute is very small compared to the size of the solvent, then its velocity is completely decoupled from the density mode of the solvent and it is the direct collision part which determines the friction on the solute.

The diffusion coefficient (D) of a particle is given by the Einstein relation,

$$D = \frac{k_B T}{m \zeta}, \quad (1)$$

where ζ is the friction on the particle having mass m . The calculation of this friction is highly nontrivial. Here we calculate it by using the renormalized kinetic theory (RKT).

The final expressions obtained by using RKT are essentially identical to those given by the standard mode-coupling theory. The microscopic expression for friction on a tagged particle is given by the following *exact* expression:

$$\zeta(z) = \frac{1}{k_B T m V} \int d_1 \dots d_2' [\hat{\mathbf{q}} \cdot \nabla_{\mathbf{r}_1} v_{12}(\mathbf{r}_1 - \mathbf{r}_2)] \times G^s(12; 1'2', z) [\hat{\mathbf{q}} \cdot \nabla_{\mathbf{r}_1'} v_{12}(\mathbf{r}_1' - \mathbf{r}_2')], \quad (2)$$

where the four-point function $G^s(12; 1'2', t')$ describes the correlated motion of the tagged particle and the solvent particles. It describes the time dependent probability that the tagged particle moves from the position (r_1', p_1') at t' to position (r_1, p_1) at t and a solvent particle which 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 $G^s(12; 1'2')$. z is the Laplace frequency, $G^s(12; 1'2', z)$ is obtained by the usual Laplace transformation of $G^s(12; 1'2', t)$.

By using the separation of time scales between the binary collision and the repeated recollisions, the above exact expression of the friction can be decomposed into a short time and a long time part. The resulting expression is given by

$$\zeta(z) = \zeta_D(z) + \zeta_R(z), \quad (3)$$

where $\zeta_D(z)$ is the short time part of the friction which arises due to direct collision between the solute and the solvent particle, and $\zeta_R(z)$ is the long time part which arises due to the correlated recollision of the solute particle with the solvent particles. Note that decomposition (3) is a standard procedure in the kinetic mode-coupling theory treatments of liquid and is known to be fairly accurate. We next describe the calculation of the direct collision term and the recollision friction.

A. Calculation of the direct collision term

We are interested here only in the zero frequency value of the friction in dense liquids. In this calculation we have replaced $\zeta_D(z=0)$ by the Enskog value for the friction $[\zeta_E = 8/3 m \sqrt{2} \pi \mu k_B T (\rho \sigma_{12}^2 g_{12}(\sigma_{12}))^7]$ where $g_{12}(\sigma_{12})$ is the value of the radial distribution function at contact. μ is the reduced mass. m is the mass of the solvent. $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, where σ_1 and σ_2 are the diameters of the solvent and the solute molecule, respectively. This substitution is reliable for the present purpose as in high density limit the repulsive part of the intermolecular potential dominates the structure and the dynamics. The thermodynamic perturbation theory^{8,9} has been used to find the reference hard sphere diameter and the density corresponding to the given Lennard-Jones system. The Enskog friction is calculated with these values. The validity of this procedure was further checked by explicitly calculating the value of $\zeta_D(z=0)$ from its more involved microscopic expression.¹⁰

For the reduced density 0.844 and the reduced temperature 0.75, we find that $\zeta_D(z=0) = 13.17$ while $\zeta_E = 13.18$.

The agreement is satisfactory for the present purpose (the values presented here are all scaled by $\tau_0 = \sqrt{m\sigma_1^2/k_B T}$).

B. Calculation of the recollisional friction

The calculation of the recollisional term is highly non-trivial. This term is obtained by expanding the total friction in the basis set of the eigen functions of the Liouville operator. The hydrodynamic modes are the natural choice of the basis set as they are the slowly decaying dynamic variables. Among all five hydrodynamic modes, the density mode and the transverse current mode of the solvent make the most important contribution. The derivation of the final expression of $\zeta_R(z)$ is lengthy and complex. Such a derivation was carried out by Sjogren and Sjolander for neat liquids.¹⁰ We have extended the calculation for a binary system, where one of the component can be different in size from the other. Taking the concentration of one of the components in the zero limit, the final expression of $\zeta_R(z)$ is given by

$$\zeta_R(z) = R_{\rho\rho}(z) - [\zeta_D(z) + R_{\rho\rho}(z)]R_{TT}(z)\zeta(z). \quad (4)$$

In the above expression, $R_{\rho\rho}(z)$ gives the coupling of the solute motion to the density modes of the solvent through the two-particle direct correlation function. $R_{TT}(z)$ gives the coupling to the transverse current through the transverse vertex function. $R_{\rho\rho}(z)$ and $R_{TT}(z)$ are obtained through the Laplace transformation of $R_{\rho\rho}(t)$ and $R_{TT}(t)$, respectively. The expressions for $R_{\rho\rho}(t)$ and $R_{TT}(t)$ are given by

$$R_{\rho\rho}(t) = \frac{\rho k_B T}{m} \int [d\mathbf{q}'/(2\pi)^3] (\hat{q} \cdot \hat{q}')^2 q'^2 [c_{12}(q')]^2 \times [F^s(q', t) - F^o(q', t)] F(q', t), \quad (5)$$

$$R_{TT}(t) = \frac{1}{\rho} \int [d\mathbf{q}'/(2\pi)^3] [1 - (\hat{q} \cdot \hat{q}')^2] [\gamma'_{d12}(q')]^2 \times \omega_{o12}^{-4} [F^s(q', t) - F^o(q', t)] C_{tt}(q', t). \quad (6)$$

The input parameters needed to calculate $R_{\rho\rho}(t)$ are the two-particle direct correlation function of the solute-solvent mixture, $c_{12}(q)$, the dynamic structure factor of the solute, $F^s(q, t)$, the inertial part of the dynamic structure factor of the solute, $F^o(q, t)$ and the dynamic structure factor of the solvent, $F(q, t)$. Similarly, the input parameter needed to calculate $R_{TT}(t)$ is the vertex function of the solute-solvent mixture, $\gamma'_{d12}(q)$, which actually takes care of the interaction of the solute motion with the current mode of the solvent. The other parameters required are the Einstein frequency of the solute in presence of the solvent molecules, ω_{o12} , the dynamic structure factor of the solute, and the transverse current autocorrelation function of the solvent, $C_{tt}(q, t)$.

Thus, in order to solve all the above equations one needs to calculate a large number of dynamical variables. The expressions of these variables are presented in the Appendix.

Finally, note that the expression for the recollision friction given by Eq. (4) involves the full friction itself on the right-hand side. Thus, the equations are to be solved self-

consistently. This is achieved by substituting the expression of $\zeta_R(z)$ in Eq. (3). The final expression of the total friction is now given by,

$$\frac{1}{\zeta(z)} = \frac{1}{\zeta_D(z) + R_{\rho\rho}(z)} + R_{TT}(z). \quad (7)$$

A merit of Eq. (7) is that it can, in principle, describe the crossover from the collision and density dominated regime to the transverse current dominated regime when the size of the solute is increased. This is demonstrated later.

It is curious to note that in certain limits the present formulation provides a microscopic justification of a semi-empirical expression of friction given by Hynes, Kapral, and Weinberg¹¹ many years ago. These authors attempted to include the microscopic effects of the friction by dividing the contribution of the solvent in two parts. The microscopic contribution arises from the friction produced by an assumed microscopic boundary layer around the tagged particle. This is given by ζ_c . Beyond this layer the contribution to the friction is considered to be given by the hydrodynamic Stokes result denoted as ζ_h . The total friction was given by the following rather unusual form

$$\frac{1}{\zeta} = \frac{1}{\zeta_c} + \frac{1}{\zeta_h}. \quad (8)$$

If in Eq. (7) we neglect the contribution from the density mode, we recover a form which is identical to that given by Hynes, Kapral, and Weinberg [Eq. (8)]. Note that while comparing the above equation with Eq. (7), ζ_c may be approximated by ζ_D for hard-sphere-like systems and R_{TT}^{-1} is equal to ζ_h in the hydrodynamic regime. The above authors have also found that the microscopic part may contribute more than 40% to the total friction. This clearly invalidates the basic assumptions behind the SE relation and deserves further study. We shall return to this point later.

III. RESULTS

We have carried out a detailed calculation of the size dependence of the diffusion coefficient. The size of the solute is varied from $\frac{1}{20}$ times to 12 times that of the solvent. The study has been carried out in two parts. The first part deals with solute smaller in size than the solvent. Here we have compared the results with the existing computer simulation results. In the second part we have studied solutes which are larger than solvents. Here we have shown the crossover from the collision and density dominated region to the transverse current dominated region.

A. Solute size smaller than solvent

We have considered diffusion in the Lennard-Jones (6-12) system with reduced temperature $T^* = 0.75$ and reduced density between $\rho^* = 0.844$ and 0.92. The calculated self-diffusion coefficient of the bulk liquid at $\rho^* = 0.844$ and $T^* = 0.728$ is equal to $1.97 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is close to the simulated values $1.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.¹² The mass of the solute is the same as the solvent molecules. This is precisely the system studied in computer simulations.⁵ The variation of

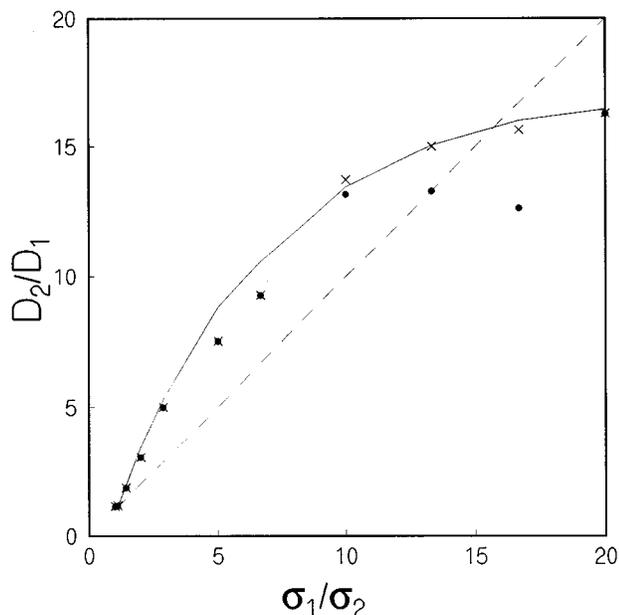


FIG. 1. The ratio of the self-diffusion coefficient of the solute (D_2) to that of the solvent molecules (D_1) is plotted as a function of the solvent-solute size ratio (σ_1/σ_2) for equal mass. The solid line represents the values calculated from the present mode coupling theory. The filled circles and the crosses represent the computer simulated (Ref. 5) and the modified computer simulated values, respectively. For comparison we have also shown the results predicted by the Stokes-Einstein relation (represented by the dashed line). Here the range of density studied is $\rho^*(=\rho\sigma^3)=0.85-0.92$ and $T^*(=k_B T/\epsilon)=0.75$.

the self-diffusion coefficient with the solute size is shown in Fig. 1, where the size of the solute molecule has been varied from 1 to $\frac{1}{20}$ times that of the solvent molecule. In the same figure we show the comparison of the calculated results with the computer simulated values.⁵ The agreement is very good. The following comments on this comparison are in order: (i) There is an enhanced diffusion at size ratios \mathcal{R} ($\mathcal{R}=\sigma_1/\sigma_2$) between 1.5 and 15. This occurs due to rather sharp *decoupling* of the solute's motion from the density modes of the solvent in this region. To get a measure of this decoupling we give below a few values of the Enskog contribution (ζ_E) and the contribution from the density mode of the solvent [$R_{\rho\rho}(z=0)$] (the values presented here are all scaled by τ_0). For same size of the solute and the solvent ($\mathcal{R}=1$), $\zeta_E=13.18$ and $R_{\rho\rho}(z=0)=10.512$. For $\mathcal{R}=2$, $\zeta_E=6.855$ and $R_{\rho\rho}(z=0)=2.39$. On the other hand, for $\mathcal{R}=5$ and above, $R_{\rho\rho}(z=0)$ becomes negligible compared to the binary part. This sharp decoupling also explains the saturation for $\mathcal{R}>10$. (ii) There is an apparent disagreement between the theory and simulation between $\mathcal{R}=12$ and 18. While the theory gives a smooth curve, there is a dip in the simulation result. We have studied the system in the limit of the solute concentration zero. So in our case the size of the solute should not influence the diffusion of the bulk solvent. It should remain constant for a particular density and temperature as the solute size is varied. We have tried to make the simulation system comparable with our studied system by fixing the value of the diffusion of a solvent molecule in

presence of other solvent molecules, $D_1=0.024$ for $\rho^*=0.92$. This leads to a smooth curve shown in Fig. 1. The agreement between theory and simulations is now excellent.

One interesting point to be noted is that for $\mathcal{R}=1$ (when the solute is of the same size as the solvent) more than 50% contribution to the friction at high density comes from the direct collision term. It shows that even such zero frequency quantity as the diffusion coefficient may receive a significant microscopic contribution. This is in agreement with the earlier observation by Hynes, Kapral, and Weinberg.¹¹ However, note that for $\mathcal{R}=1$ we find the hydrodynamic contribution to the friction to be negligible.

B. Solute size larger than solvent

We next address the interesting question of the crossover to the SE behavior for large solutes. In the regime where the solute size is bigger than the size of the solvent, the diffusion mechanism can be completely different. In this limit one expects a hydrodynamic behavior and the SE relation to be valid. Earlier studies¹³ show that Eq. (7), with only the $R_{TT}(z)$ term, can correctly reduce to the SE limit for large σ_2/σ_1 , provided that $F^s(q,t)$ is set to unity, $F^0(q,t)$ is neglected, and the vertex function has the proper form which was, however, left unspecified. No detailed study of this problem, to the best of our knowledge, has ever been carried out for dense liquids. We consider the following questions particularly interesting: Where exactly the crossover takes place? Is there any sharp crossover at all? Since we are interested in large solute sizes, $F^0(q,t)$ is neglected. This further guarantees that $R_{TT}(z)$ has the correct hydrodynamic form. We have studied the relative values of $1/[\zeta_D(z)+R_{\rho\rho}(z)]$ and $R_{TT}(z)$ which are calculated self-consistently. In Fig. 2 we have plotted the size ratio dependence of the values of the first term and the second term of Eq. (7). We see that value of $R_{TT}(z)$ is higher than $1/\zeta_D(z)+R_{\rho\rho}(z)$ when σ_2/σ_1 is 3 and above. The scenario changes below size ratio 3 and $R_{TT}(z)$ rapidly becomes smaller as we approach size ratio 1. When $\mathcal{R}^{-1}\geq 4$, the magnitude of $\zeta(z=0)$ increases almost linearly with the size of the solute. The ratio $m\zeta(z=0)/\eta R$, which can be termed the hydrodynamic boundary coefficient (HBC), is equal to 12.545 for $\mathcal{R}^{-1}=4$, which is very close to 4π , the value of the slip HBC. We were also curious to know the effect of the inertial term [$F^0(q,t)$] on the crossover. With this term present in R_{TT} we found that the crossover takes place at somewhat larger solute size $\sigma_2/\sigma_1\approx 6$. However, the ratio $m\zeta(z=0)/\eta R$ remains large, which is rather unphysical. The effect of $F^0(q,t)$ on the diffusion of solute for larger sizes requires further study.

A study of the crossover has also been carried out by considering the mass dependence of the solutes of different sizes. It is known that for inert gasses and alkanes the mass varies almost linearly with the diameter.^{8,14} Considering this, we calculated the values of $1/\zeta_D(z)+R_{\rho\rho}(z)$ and $R_{TT}(z)$. The results obtained are not significantly different, reflecting the relative insensitivity of diffusion to the mass. In this case the crossover shifts to a slightly larger size ratio.

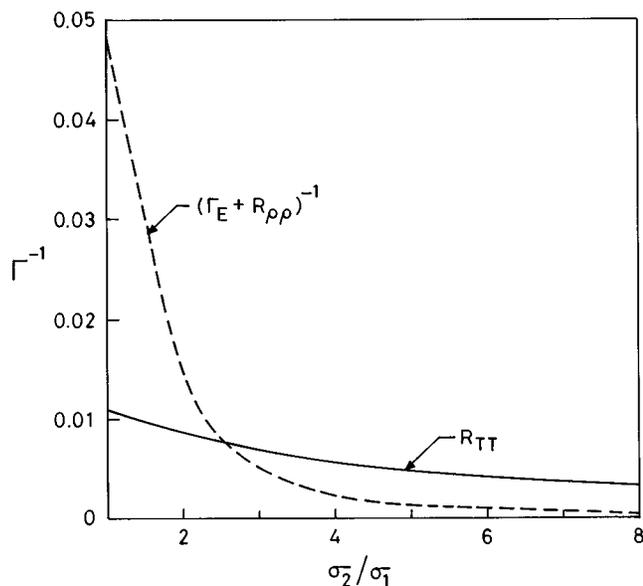


FIG. 2. The size mediated crossover from the microscopic to the hydrodynamic behavior of diffusion. In this figure the contribution to the diffusion from the binary and the density modes given by $[\zeta_D + R_{\rho\rho}]^{-1}$ has been compared with that from the transverse current mode given by R_{TT} . All the values are scaled by $\tau_0 = [m\sigma^2/k_B T]^{1/2}$.

It is found that the total friction is higher in this case which is expected.

IV. CONCLUSION

After summarizing the results, the following physical picture of the size dependence of diffusion emerges from the present study. In dense liquids the relative importance of the hydrodynamic modes of the solvent in the motion of a solute particle is determined largely by the solute–solvent size ratio. When the size of the solute is decreased from a very large value (where the hydrodynamic SE relation is valid) the combination $(\zeta_D + R_{\rho\rho})$ (the combined effect of the binary collision and the density modes) decreases rapidly which, in turn, leads to the breakdown of the hydrodynamic behavior. The density term itself, $R_{\rho\rho}$, is most important when the solute–solvent size ratio is about two. If we further decrease the size of the solute, then the density mode also becomes irrelevant and it is only the binary part which contributes to the friction on the tagged particle.

From the above study we find that for normal liquids and for the same solute–solvent size ratio, the direct collision part contributes more than 50% to the total friction. This picture is expected to change in supercooled liquids. In this regime the structural relaxation of the solvent becomes very slow, which causes the friction to increase rapidly as the liquid is progressively supercooled. Although the number of direct collisions will undergo a modest increase due to the increase in the number of nearest neighbors, it is the coupling of the solute motion to the density fluctuation which is expected to make the dominant contribution. In the supercooled regime the natural flow of the solvent also becomes very slow. As both the structural relaxation and the flow of

the natural current of the solvent slow down, the position of crossover might shift as the size of the solute is varied. In the deeply supercooled regime the picture may change again. Here the density fluctuation becomes so slow that diffusion occurs through an activated hopping mechanism, the origin of which is not yet clearly understood. The present formulation cannot be applied to describe this regime.

An interesting result of the present study is the recovery of the Stokes expression between the friction and the viscosity. An intriguing aspect is the natural convergence of the ratio $m\zeta(z=0)/\eta R$ to the slip hydrodynamic boundary coefficient (HBC) as the solute size is increased. This then naturally raises the question that, what are the conditions under which the stick HBC, 6π , can be recovered. In our calculation we have considered the LJ energy parameter of the solute–solvent pair (ϵ_{12}) equal to that of solvent–solvent pair (ϵ). We think that an appropriate calculation would be to study the dependence of the friction as a function of (ϵ_{12}/ϵ) . When $\epsilon_{12} > \epsilon$, the value of the friction on the solute particle is expected to increase as the solute experiences a greater attraction toward its neighboring solvent molecules. This rise in the friction might lead to the stick HBC. We hope to address this problem in the future.

In conclusion, the results presented here show, for the first time, that the known enhancement of diffusion for small solute sizes can be explained from first principles. In addition, we predict that the crossover from the microscopic to the hydrodynamic regime should occur when the solute is about 2–3 times larger than the solvent molecules. The present study also suggests that the decoupling of the solute motion from the solvent hydrodynamic modes is hierarchical. However, the quantitative details may again change when the liquid is in the supercooled regime.

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APPENDIX

Here we present the calculational details of all the input parameters required to calculate $R_{\rho\rho}(t)$ and $R_{TT}(t)$.

In Eq. (5), $c_{12}(q)$ is the two-particle direct correlation function between the solute and the solvent molecules in the wave vector (q) space and it is calculated by using the well-known WCA theory which requires the solution of the Percus–Yevick equation for the binary mixture.¹⁵ The latter is obtained after taking the limit of solute concentration zero. $F^S(q, t)$ is the self-dynamic structure factor which is assumed to be given by^{7,9,16}

$$F^s(q, t) = \exp \left[\frac{-q^2 k_B T}{m \zeta_0} \left(t + \frac{1}{\zeta_0} (e^{-t \zeta_0} - 1) \right) \right], \quad (\text{A1})$$

where $\zeta_0 = \zeta(z=0)$, the latter has been calculated self-consistently from Eq. (7).¹² In the expression of $F^s(q, t)$ using the zero frequency value of the friction is an approximation. It is the time dependent friction which would have given us the correct result; but doing an infinite-loop calculation with the time dependent friction is nearly impossible. Assuming the zero frequency limit does not introduce much error, we know that the major contribution of $R_{\rho\rho}(t)$ to the total friction is in the long time limit. $F^0(q, t)$ is the inertial part of the self-dynamic structure factor given by

$$F^0(q, t) = \exp \left(-\frac{k_B T}{m} \frac{q^2 t^2}{2} \right). \quad (\text{A2})$$

$F(q, t)$ is the dynamic structure factor of the solvent. It is obtained from its Laplace transform from $F(q, z)$. By using the following well-known Mori continued-fraction expansion and truncating at second order, the expression for $F(q, z)$ can be written as^{7,12}

$$F(q, z) = \frac{S(q)}{z + \frac{\langle \omega_q^2 \rangle}{\Delta q}} \frac{1}{z + \frac{\Delta q}{z + \tau_q^{-1}}}, \quad (\text{A3})$$

where $S(q)$ is the static structure factor. The static structure factor is calculated from the solution of the Percus–Yevick equation for pure liquids.⁹ $\langle \omega_q^2 \rangle = (k_B T q^2) / m S(q)$ and $\tau_q^{-1} = 2 \sqrt{\Delta q} / \pi$. $\Delta q = \omega_l^2(q) - \langle \omega_q^2 \rangle$, where $\omega_l^2(q)$ is the second moment of the longitudinal current correlation function given by^{7,12}

$$\omega_l^2(q) = 3q^2 \frac{k_B T}{m} + \omega_0^2 + \gamma_d^l(q). \quad (\text{A4})$$

Here $\gamma_d^l(q)$ is the longitudinal component of the vertex function and ω_0 is the well-known Einstein frequency of the solvent,

$$\gamma_d^l(q) = -\frac{\rho}{m} \int d\mathbf{r} \exp(-i\mathbf{q} \cdot \mathbf{r}) g(r) \frac{\delta^2}{\delta z^2} v(r), \quad (\text{A5})$$

$$\omega_0^2 = \frac{\rho}{3m} \int d\mathbf{r} g(r) \nabla^2 v(r). \quad (\text{A6})$$

$g(r)$ is the radial distribution function and $v(r)$ is the interatomic potential of the solvent. It is known that Eq. (A3) provides a reliable description of $F(q, z)$ over the whole (q, z) plane.

In Eq. (6), $\gamma_{d12}^l(q)$ is the tangential component of the vertex function and ω_{012} is the Einstein frequency of the solute–solvent mixture. The expression of ω_{012}^2 is the same as Eq. (A6), only replacing $g(r)$ by $g_{12}(r)$ and $v(r)$ by $v_{12}(r)$. The expression for $\gamma_{d12}^l(q)$ is given by

$$\gamma_{d12}^l(q) = -\frac{\rho}{m} \int d\mathbf{r} \exp(-i\mathbf{q} \cdot \mathbf{r}) g_{12}(r) \frac{\delta^2}{\delta x^2} v_{12}(r). \quad (\text{A7})$$

We have assumed that the transverse current correlation function is given by

$$C_{tt}(q, z) = \frac{1}{z + \frac{\omega_t^2(q)}{z + \tau_t^{-1}(q)}}, \quad (\text{A8})$$

where $\omega_t^2(q)$ is the second moment of the transverse current correlation function which is given by^{7,12}

$$\omega_t^2(q) = q^2 \frac{k_B T}{m} + \omega_0^2 + \gamma_d^t(q). \quad (\text{A9})$$

Here $\gamma_d^t(q)$ is the transverse component of the vertex function which has the same expression as Eq. (A7), only replacing $g_{12}(r)$ by $g(r)$ and $v_{12}(r)$ by $v(r)$. For $\tau_t(q)$ we have used the expression proposed by Akazu and Daniels,¹⁷

$$\tau_t^{-2}(q) = 2\omega_t^2(q) + \frac{\tau_t^{-2}(0) - 2\omega_t^2(q) + 2q^2 \frac{k_B T}{m}}{1 + (q/q_0)^2}. \quad (\text{A10})$$

Here q_0 is an adjustable parameter which actually determines the transition of the behavior of $C_{tt}(q, z)$ from “small q ” to “large q .” For argon $q_0 = 1.5 \text{ \AA}^{-1}$; $\tau_t^{-1}(0) = \lim_{q \rightarrow 0} [m\rho\omega_t^2(q)]/q^2\eta$. Here η is the zero frequency shear viscosity which is calculated from the following mode coupling expression:^{18,19}

$$\eta = \eta_E + k_B T / 60\pi^2 \int_0^\infty dq q^4 [S'(q)/S(q)]^2 \times \int_0^\infty dt [F(q, t)/S(q)]^2. \quad (\text{A11})$$

Here $S'(q)$ is the first derivative of the static structure factor. η_E is the Enskog shear viscosity given by¹⁸

$$\eta_E = \eta_B \frac{(1 + 3.2\phi g_{12}(\sigma_{12}) + 12.18\phi^2 g_{12}^2(\sigma_{12}))}{g_{12}(\sigma_{12})}, \quad (\text{A12})$$

where $\phi = \pi\rho^*/6$ and $\eta_B = 0.179(mk_B T)^{1/2}/\sigma^2$. We have compared the value of viscosity calculated from the above expression with simulation results.²⁰ The agreement is good. For example, at $T^* (= k_B T/\epsilon) = 0.728$ and $\rho^* (= \rho\sigma^3) = 0.844$, $\eta(\text{simulation}) = 2.53$ and $\eta(\text{calculated}) = 2.77$. Here σ and ϵ are the usual Lennard–Jones parameters for the diameter and well depth, respectively. The values of η are scaled by $(mk_B T)^{1/2}/\sigma^2$. Equation (A8), after using the proper value of q_0 , provides a satisfactory description of the transverse current fluctuations over a wide range of wavelength. All the microscopic equations given above are fully self-contained and are solved self-consistently.

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