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# Molecular theory of nonpolar solvation dynamics

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Recently Berg and co-workers have reported interesting time resolved studies of ultrafast solvation dynamics in a completely nonpolar liquid. The relevant time correlation function was found to exhibit many fascinating properties. It was biphasic and highly nonexponential in the supercooled liquid near the glass transition temperature. In this article we present a general microscopic theory of such solvation phenomena. It is found that in contrast to solvation of charged species in polar solvents, the nonpolar solvation dynamics is controlled essentially by the dynamic structure factor of the liquid; the orientational relaxation is seen to play a less important role. As the dynamic structure factor shows anomalous behavior in the supercooled liquid, so does the solvation time correlation function. The theory suggests that nonpolar solvation dynamics can be an *important* scale dependent probe of microscopic dynamical processes in the supercooled liquid.

## I. INTRODUCTION

Over the last decade intensive studies of solvation dynamics of newly created charge species in polar solvents have contributed much to our understanding of molecular dynamics in dense complex liquids.<sup>1</sup> In a dipolar liquid, the solvation dynamics is controlled essentially by the orientational motion of the dipolar molecules, although the translational motion often contributes significantly to accelerate the process. Another important factor in polar solvation dynamics is the long range nature of the polar interactions which is directly responsible for making solvation dynamics of an ion much faster than the single particle orientation. However, the above two factors also make polar solvation dynamics sensitive primarily to the long wavelength or the macroscopic properties of the liquid—microscopic aspects of structural relaxation in a dense liquid are not always significantly probed by polar solvation. This is somewhat unfortunate because an understanding of microscopic structural relaxation is necessary to understand solvent effects on chemical reactions.

This situation seems to have improved with the recent work of Berg and co-workers<sup>2-4</sup> who measured time resolved dynamics of solvation of excited nonpolar solute dimethyl-*s*-tetrazene in nonpolar solvent *n*-butylbenzene. Since the coupling between the solute and the solvent is short ranged, these experiments essentially probed the molecular length scale dynamics of the host liquid. A very important aspect of this study is that temperature was varied over a rather large range, spanning five orders of magnitude of the viscosity values. The results of this study reveals many interesting aspects of the solvation dynamics of a nonpolar solute in a nonpolar solvent. As found for polar solvents,<sup>1</sup> the dynamics in this case also separate into a phonon modulated and a structural component, the former persists in the low temperature glass while the latter is present only in the liquid phase. The relaxation was biphasic and strongly nonexponential in the supercooled liquid. This nonexponentiality ex-

tends over several orders of magnitude in time and be fitted to a stretched exponential form with values of the stretched exponentiality parameter  $\beta$  between 0.3 and 0.5. Another important result is the dependence of the dynamics on the nature of the solute-solvent coupling—while the slow structural part of the relaxation seems to exhibit a linear coupling, the situation is more complicated for the phonon part.

Although many aspects of nonpolar solvation dynamics can be understood qualitatively,<sup>2-4</sup> it seems worthwhile to have a microscopic theory which incorporates all the essential features of the relaxation and which thus helps in making the relevant discussion quantitative. The objective of this article is to present such a theory. The theory that we use can be considered a time dependent Ginzburg-Landau (TDGL) theory. The approach adopted here was pioneered by Munakata.<sup>5</sup> In this theory a microscopic expression for the time dependent potential energy of a solute is expressed in terms of an effective interaction between the solute and the solvent and fluctuating density of the liquid. This approach naturally leads to an expression for the energy time autocorrelation function (ETCF) which, within the linear response assumption, is the quantity measured in the solvation dynamics experiments.<sup>2</sup> This energy time correlation function has rather interesting structure. It relates the ETCF to an integration over the dynamic structure factor,  $F(k,t)$ , of the nonpolar solvent. The theory provides a simple explanation of the observed biphasic (phononlike and structural) behavior of solvation. Moreover, this theory suggests that the ETCF will be quite sensitive to the short wavelength structural relaxations observed in fragile liquids, like butylbenzene. Nonexponentiality of ETCF arises naturally in the present theory. An important prediction of the theory is that nonpolar solvation dynamics can be a good probe of local density relaxations which are expected to play important role in chemical dynamics in solution. We also present numerical results.

The organization of the rest of the article is as follows. In the next section we present the theoretical formulation. In Sec. III, numerical results are presented. Section IV con-

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cludes with a discussion of the theory its limitations and future applications.

## II. THEORY

We shall use the well-known density functional theory<sup>6-8</sup> to derive an expression for the effective potential energy of a tagged molecule in dense liquids. As mentioned earlier, Munakata<sup>5</sup> has presented an elegant approach based on the linear response of the medium; the approach adopted here was discussed earlier in a different context.<sup>7,8</sup> The starting point is the density functional theory expression for the free energy functional  $F(\mathbf{r}, \mathbf{\Omega}, t)$  which is a function of the position ( $\mathbf{r}$ ) and orientation ( $\mathbf{\Omega}$ ) dependent density,  $\rho_i(\mathbf{r}, \mathbf{\Omega})$ , of the  $i$ th component in an  $n$ -component mixture. This expression is given by<sup>7,8</sup>

$$\begin{aligned} \beta F[\rho_i(\mathbf{r}, \mathbf{\Omega})] &= \int d\mathbf{r} d\mathbf{\Omega} \sum_i \rho_i(\mathbf{r}, \mathbf{\Omega}) [\ln \rho_i(\mathbf{r}, \mathbf{\Omega})^{-1}] \\ &\quad - \frac{1}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{\Omega} d\mathbf{r}' d\mathbf{\Omega}' [\rho_i(\mathbf{r}, \mathbf{\Omega}) - \rho_i^0/4\pi] \\ &\quad \cdot [\rho_j(\mathbf{r}, \mathbf{\Omega}) - \rho_j^0/4\pi] C_{ij}(\mathbf{r} - \mathbf{r}', \mathbf{\Omega}, \mathbf{\Omega}'), \end{aligned} \quad (1)$$

where  $\beta = (k_B T)^{-1}$ ,  $k_B T$  is Boltzman constant times the temperature, and  $\rho_i^0$  is the equilibrium number density of species  $i$ .  $C_{ij}(r_i, \Omega_i, r_j, \Omega_j)$  is the two particle direct correlation function between a molecule of species  $i$  and one of species  $j$  at positions  $r_i$  and  $r_j$  with orientations  $\Omega_i$  and  $\Omega_j$ , respectively. The sum in Eq. (1) is over all the species in the system. The direct correlation functions  $C_{ij}$  contain detailed microscopic information about the spatial and the orientational intermolecular correlations of the molecular liquid. In order to find the expression for the effective potential on a tagged molecule of species  $i$ , we take the derivative of the free energy with respect to the density of that species

$$\begin{aligned} \frac{\delta \beta F}{\delta \rho_i} &= \ln[\rho_i(\mathbf{r}, \mathbf{\Omega})] - \sum_j \int d\mathbf{r}' d\mathbf{\Omega}' C_{ij} \\ &\quad \times (\mathbf{r} - \mathbf{r}', \mathbf{\Omega}, \mathbf{\Omega}') [\rho_j(\mathbf{r}', \mathbf{\Omega}') - \rho_j^0/4\pi]. \end{aligned} \quad (2)$$

At equilibrium, the derivative of the free energy with respect to density is zero. So, we obtain the following expression for the density field:

$$\rho_i^{\text{eq}}(\mathbf{r}, \mathbf{\Omega}) = \frac{\rho_i^0}{4\pi} \exp[-\beta V_{\text{eff}}^{(i)}(\mathbf{r}, \mathbf{\Omega})], \quad (3)$$

where

$$\begin{aligned} \beta V_{\text{eff}}^{(i)}(\mathbf{r}, \mathbf{\Omega}) &= - \sum_j \int d\mathbf{r}' d\mathbf{\Omega}' C_{ij}(\mathbf{r} - \mathbf{r}', \mathbf{\Omega}, \mathbf{\Omega}') \\ &\quad \cdot [\rho_j(\mathbf{r}', \mathbf{\Omega}') - \rho_j^0/4\pi]. \end{aligned} \quad (4)$$

Equation (4) can be generalized to the time domain to obtain an expression for time dependent effective potential energy

$$\begin{aligned} \beta V_{\text{eff}}^{(i)}(\mathbf{r}, \mathbf{\Omega}, t) &= - \sum_j \int d\mathbf{r}' d\mathbf{\Omega}' C_{ij}(\mathbf{r} - \mathbf{r}', \mathbf{\Omega}, \mathbf{\Omega}') \\ &\quad \cdot \delta \rho_j(\mathbf{r}', \mathbf{\Omega}', t), \end{aligned} \quad (5)$$

where  $\delta \rho_j(\mathbf{r}, \mathbf{\Omega}, t) = \rho_j(\mathbf{r}, \mathbf{\Omega}, t) - \rho_j^0/4\pi$  is the fluctuation in position, orientation, and time dependent number density.

In the experimental situation, the concentration of solute molecules is very small. In addition, we are interested in a solvent of one component system here. Therefore, the effective potential energy is given by

$$\begin{aligned} \beta V_{\text{eff}}^{(2)}(\mathbf{r}, \mathbf{\Omega}, t) &= - \int d\mathbf{r}' d\mathbf{\Omega}' C_{21}(\mathbf{r} - \mathbf{r}', \mathbf{\Omega}, \mathbf{\Omega}') \\ &\quad \times \delta \rho_1(\mathbf{r}', \mathbf{\Omega}', t), \end{aligned} \quad (6)$$

where  $C_{21}(r - r', \Omega, \Omega')$  is now the direct correlation function between the probe solute (labeled 2) and the solvent molecules (labeled 1). Equation (6) relates the fluctuation in the effective potential energy to the fluctuation in number density. This is certainly a valid representation in a dense liquid.

Let us now denote the energy-energy time correlation function (ETCF) by  $C_{\text{EE}}(t)$ . If we assume that the solute probe is immobile, then the position of the solute remains fixed during the relaxation of its energy and we can take this position as the origin of the coordinate system. However, we must average over this position and also the orientation of the solute as they are arbitrary. Therefore,  $C_{\text{EE}}(t)$ , is given by the following expression:

$$C_{\text{EE}}(t) = \frac{1}{4\pi V} \int d\mathbf{r} d\mathbf{\Omega} \langle V_{\text{eff}}^{(2)}(\mathbf{r}, \mathbf{\Omega}, t=0) V_{\text{eff}}^{(2)}(\mathbf{r}, \mathbf{\Omega}, t) \rangle, \quad (7)$$

where  $\langle \dots \rangle$  denotes averaging over an equilibrium ensemble and  $V$  is the volume of the system.

The following steps are now followed to reduce Eq. (7) to a tractable form.

- (1) We assume a dynamic linear response of the solvent. This is equivalent to the assumption that the solvent is not significantly perturbed by the solute. This is a standard approximation. If the solute is mobile, then Eq. (7) would lead to the familiar cumulant approximation of the four time correlation function, well-known in molecular hydrodynamics.<sup>9</sup>
- (2) We switch over to the Fourier representation with  $\mathbf{k}$  as the wave vector conjugate to  $r$  by using the following transformation:

$$f(\mathbf{k}) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) f(\mathbf{r}). \quad (8)$$

Equation (6) then gives the following wave vector dependent expression for the effective potential energy of the solute

$$\beta V_{\text{eff}}^{(2)}(\mathbf{k}, \mathbf{\Omega}, t) = - \int d\mathbf{\Omega}' C_{21}(\mathbf{k}, \mathbf{\Omega}, \mathbf{\Omega}') \delta \rho_1(\mathbf{k}, \mathbf{\Omega}, t). \quad (9)$$

- (3) Next, the direct correlation function  $C_{21}(\mathbf{k}, \mathbf{\Omega}, \mathbf{\Omega}')$  is expanded in spherical harmonics

$$C_{21}(\mathbf{k}, \mathbf{\Omega}, \mathbf{\Omega}') = \sum_{l_1 l_2 m} C_{21}(l_1, l_2, m; k) Y_{l_1 m}(\mathbf{\Omega}) Y_{l_2 m}(\mathbf{\Omega}'), \quad (10)$$

where  $\mathbf{k}$  is taken parallel to the  $z$ -axis.

- (4) Similarly,  $\delta\rho(\mathbf{k}, \mathbf{\Omega}, t)$  is also expanded in the spherical harmonics

$$\delta\rho_1(\mathbf{k}, \mathbf{\Omega}, t) = \sum_{l, m} a_{lm}^{(1)}(\mathbf{k}, t) Y_{lm}(\mathbf{\Omega}). \quad (11)$$

- (5) Equations (9), (10), and (11) are now substituted in Eq. (7) to obtain the following expression for the energy time correlation function:

$$C_{EE}(t) = \frac{\beta}{96\pi^4} \int d\mathbf{k} \sum_{l_1 l_2 m} (-1)^m C_{21}^2(l_1 l_2 m; k) \cdot \frac{1}{V} \langle a_{l_2 m}^{(1)}(-\mathbf{k}, t=0) a_{l_2 m}^{(1)}(\mathbf{k}, t=0) \rangle. \quad (12)$$

- (6) We now define the intermediate scattering function  $F_{lm}(k, t)$  as

$$F_{lm}^{(1)}(k, t) = \frac{1}{V} \langle a_{lm}^{(1)}(-\mathbf{k}, t=0) a_{lm}^{(1)}(\mathbf{k}, t) \rangle. \quad (13)$$

Note that the dynamic structure factor,  $S_{lm}(\mathbf{k}, \omega)$  is the Laplace transform of the intermediate scattering function

$$S(k, \omega) = \int_0^\infty dt \exp(i\omega t) F(k, t).$$

All the above steps lead to the following expression for  $C_{EE}(t)$ :

$$C_{EE}(t) = \frac{k_B T}{6\pi^2 \rho} \int_0^\infty dk k^2 \sum_{l_1 l_2 m} \left[ \frac{\rho_0}{4\pi} C_{21}(l_1 l_2 m j k) \right]^2 \cdot F_{l_2 m}^{(1)}(k, t). \quad (14)$$

This general expression includes contributions not only from the angle averaged spatial correlations (given by the  $l_1 = l_2 = m = 0$  component), but also from the orientational correlations given by nonzero values of  $l$  and  $m$ . The  $t=0$  limit of Eq. (14) gives the mean square fluctuation of the potential energy in terms of the static structure factors,  $S_{lm}(k) = S_{lm}(k, t=0)$ . The normalized potential energy correlation function is defined as

$$S(t) = \frac{C_{EE}(t)}{C_{EE}(t=0)}. \quad (15)$$

We shall calculate  $S(t)$  in the next section.

In polar solvation dynamics, the energy correlation function is dominated by nonzero  $l$  values. For example, if the solute is a spherical molecule with a charge at the center, then only the  $l_1 = l_2 = 1$  and  $m = 0$  term is important.<sup>8</sup> For solvation of a dipolar solute, both  $m = 0$  and  $m = 1$  terms are involved. Higher  $l$ 's can also be involved in a nonlinear

theory. However, if the solvation is dominated by nonpolar interactions, such as in the experiments of Berg,<sup>2-4</sup> then the correlation function can be dominated by the isotropic,  $l = m = 0$  term. In such a situation, the correlation function  $S(t)$  can be approximated by

$$S(t) = \frac{\int_0^\infty dk k^2 C_{21}^2(k) F(k, t)}{\int_0^\infty dk k^2 C_{21}^2(k) S(k)}, \quad (16)$$

where  $C_{21}(k) = (\rho_0/4\pi) C_{21}(000; k)$ ,  $F(k, t) = F_{00}^{(1)}(k, t)$  and  $S(k)$  is the usual static structure factor of the host liquid. Equation (16) is an important result of this article. The important aspect of Eq. (16) is that it relates the correlation function  $S(t)$  to the dynamic structure factor of the solvent,  $S(k, \omega)$ . The direct correlation function  $C_{21}(k)$  is essentially the wave vector (or scale) dependent coupling between the solute and the host solvent.

Equation (16) shows that the correlation function  $S(t)$  derives contributions from dynamical processes occurring at all length scales. In fact, many nontrivial conclusions can be drawn directly from Eq. (16) if one exploits the known facts about  $F(k, t)$  and  $C_{21}(k)$ . At high temperature or low density, the time dependence of the intermediate scattering function is exponential-like. At small  $k$ , it is a sum of two exponentials which gives the Rayleigh-Brillouin spectrum. At low density or high temperature, the spatial structure at molecular length scales hardly forms and the density relaxations at these length scales do not show appreciable de Gennes' narrowing.<sup>9</sup> The high frequency or short time part of  $F(k, t)$  is dominated by sound waves or the phonon modes. Here the response of the solvent is viscoelastic. The low frequency or long time response, on the other hand, is dominated by structural relaxation mediated by viscosity. Therefore, at high temperatures, solvation proceeds via the same mechanism that is responsible for shear relaxation and sound attenuation. This aspect will be made more quantitative in the next section.

The dynamics, however, changes drastically at low temperature or at high density. Now, the dynamics at molecular length scales is rather different from those at long wavelengths, so  $S(t)$  becomes nonexponential. The nonexponentiality increases further when the liquid is supercooled. At temperatures near but above the glass transition temperatures, the long times behavior of  $F(k, t)$  is markedly nonexponential and this will be reflected in  $S(t)$  also. In the glassy phase, on the other hand, structural relaxation freezes out. Here the relaxation is dominated essentially by the  $\beta$ -relaxation processes.<sup>9</sup> The relaxation will still be nonexponential. In fact, solvation dynamics of nonpolar solutes offers a unique tool to study microscopic aspects of  $\alpha$ - $\beta$  relaxation processes.

If angle dependent interactions between the solute and the solvent are important, then we must consider relaxation of orientational structure factors as well. Even in a nonpolar systems, we may have significant contribution from second rank ( $l=2$ ) coefficients. Thus, for ellipsoidal molecules, we need to consider  $S_{2m}(k, t)$  coefficients. Despite this complexity, the qualitative behavior of  $S(t)$  should remain the same.

It is of interest to contrast the dynamics of nonpolar solvation with those of polar solvation. For the solvation of

an ion in a dipolar liquid, the direct correlation function  $C_{21}(k)$  behaves as  $k^{-2}$  at low  $k$ . This cancels the  $k^2$  term on the right-hand side of Eq. (14). As a result, ionic solvation derives a big contribution from the long wavelength (that is the  $k \approx 0$ ) polarization modes. The contribution of large  $k$  modes are often not very significant (there are, of course, exceptions). Thus, the solvation dynamics of an ion may not be very sensitive to its surrounding microscopic structure. The nonpolar solvation dynamics, on the other hand, is sensitive to these details of the microscopic liquid structure.

We would like to point out that Eq. (14) provides a unified description of solvation dynamics in a dense liquid in the sense that it includes both the polar and the nonpolar solvation as the special cases. For example, for ionic solvation it correctly goes over to the known molecular hydrodynamic expression.<sup>7,8</sup>

An important aspect of Eqs. (14) and (16) is a prediction of the dependence of dynamics on the size of the solute probe. This factor enters through the correlation function  $C_{21}(k)$ . If the solute is much larger than the solvent molecules, then the long wavelength contribution will dominate the relaxation. On the other hand, for solute sizes comparable to the solvent molecular size, the molecular length scale processes can contribute significantly. If the size of the solute is much smaller than the solvent, then large  $k$  processes shall dominate, and the probe may not see much beyond the first nearest neighbors. Thus, the size of the nonpolar solute can indeed play an important role in the study of the scale dependence of relaxation in the supercooled liquid.

In the present description, the coupling between the solute probe and the host solvent is given by the direct correlation function,  $C_{21}(k)$ . Since this term enters in the quadratic form, the coupling is at least quadratic in the strength of the solute-solvent interaction. In principle, however, this coupling is more complicated as  $C_{21}(k)$  can have a strong dependence not only on the solute-solvent size ratio but also on the strength of the attractive interaction between the solute and the solvent. We next present the results of our numerical calculations.

### III. NUMERICAL RESULTS

In order to calculate the solvation time correlation function,  $S(t)$ , we need both the direct correlation function  $C_{21}(k)$  and the intermediate scattering functions,  $F(k, t)$ . The latter can be obtained from experiments. The former is more difficult, especially for molecules with complex geometries. Fortunately, however,  $C_{21}(k)$  is known analytically for a model system—that of binary mixture of hard spheres.<sup>10</sup> Since direct correlation functions are short ranged, these correlation functions from a hard sphere model are expected to be reliable for any short range intermolecular interactions, such as Lennard-Jones. Because  $C_{21}(k)$  is known analytically we can easily study the size dependence of the probe.

In Figs. 1(a), 1(b), and 1(c) we show the wave vector dependence of the function  $I(k)$  defined by  $I(k) = k^2 C_{21}^2(k) S(k)$ . The function  $I(k)$  is a measure of the relative weight of different  $k$ 's in the integrations involved in

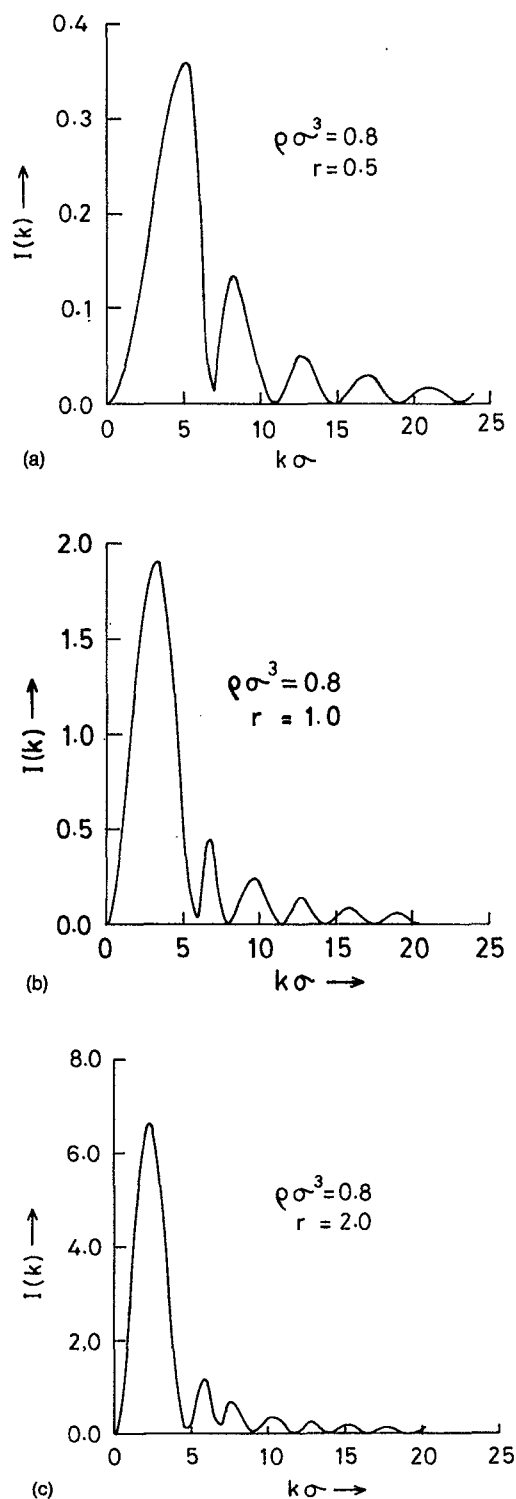


FIG. 1. The wave vector dependence of the function  $I(k)$  defined as  $I(k) = k^2 C_{21}^2(k) S(k)$  for three different values of the solute-solvent size ratio,  $r = 2a/\sigma$ , where  $a$  is the radius of the solute (assumed spherical) and  $\sigma$  is solvent diameter. (a)  $r = 0.5$ ; (b)  $r = 1.0$ ; and (c)  $r = 2.0$ . The reduced density ( $\rho^* = \rho\sigma^3$ ) of the liquid is 0.8.

Eq. (16). In the Figs. 1,  $I(k)$  has been plotted for three different values of the solute-solvent size ratio,  $r = 2a/\sigma$  (where  $a$  is the radius of the solute and  $\sigma$  is the diameter of the host molecules). It can be seen clearly that as the probe

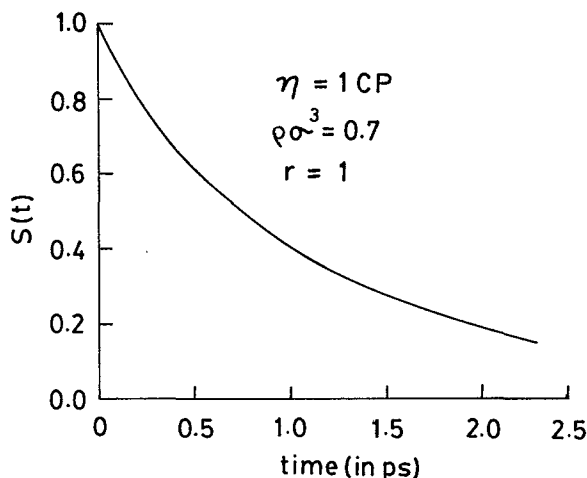


FIG. 2. The time dependence of the nonpolar solvation time correlation function  $S(t)$  at high temperatures. Here  $S(t)$  has been evaluated by using Eq. (16) and the intermediate scattering function is given by Eqs. (17) and (18) of the text, respectively. The parameter values have been discussed in the text.

size is increased the relative contribution from the small  $k$  values increases.

We next discuss the calculation of  $S(t)$ . At high temperatures, the intermediate scattering function may be approximated by the following hydrodynamic expression:<sup>11</sup>

$$F(k, t) = S(k) [G \exp(-D_T \tau k^2 t) + (1/\gamma) \cos(c_s k t) \exp(-\Gamma k^2 t)], \quad (17)$$

for small  $k$  region and

$$F(k, t) = S(k) \exp[-D_s k^2 t / S(k)]. \quad (18)$$

for the intermediate  $k$  region. We chose Eq. (17) to be valid for  $k\sigma < 1$ . In Eq. (17),  $D_T$  and  $D_s$  are the thermal and the self-diffusion coefficients, respectively,  $c_s$  is the adiabatic sound velocity,  $\Gamma$  is the sound attenuation coefficient,  $G = 1 - 1/\gamma$ , and  $\gamma$  is the ratio of specific heats. In the normal liquid, these have nearly the same values for many liquids. In order to simulate dynamics in a typical liquid we have chosen the following values.  $D_T = 10^{-2}$  cm<sup>2</sup>/s,  $D_s = 10^{-5}$  cm<sup>2</sup>/s,  $\Gamma = 10^{-2}$  cm<sup>2</sup>/s,  $c_s = 980$  m/s, and  $\gamma = 2$ .

In Fig. 2 we show the result of our calculation of  $S(t)$  at a density equal to  $\rho\sigma^3 = 0.7$  which is quite above the freezing density. The decay is very fast and exponential-like. This decay is in the subpicosecond range. This is in agreement with the experimental observations<sup>2-4</sup> that nonpolar solvation in nonpolar liquid at high temperatures can be ultrafast in the sense that the relaxation is mostly in the subpicosecond time scale.

The calculation of  $S(t)$  in the supercooled liquid range is much more complicated because the dynamical structure factor shows rich dynamics which depend not only on the wave vector  $\mathbf{k}$  but also on its proximity to the glass transition temperature. In general, the intermediate scattering function or the dynamic structure factor shows highly nonexponential dynamics in this domain. Mode-coupling theory has recently

provided an elegant description of density relaxation in the supercooled liquid that is valid at densities and/or temperatures above the true glass transition temperature.<sup>9,12</sup> Both the experiment and the mode-coupling theory shows that the scattering function is well-represented by the well-known Kohlrausch-Williams-Watts (KWW) form, but with both the relaxation time and the exponent  $\beta$  wave vector dependent. Thus the mode coupling part of the intermediate scattering function is given by

$$F_{MC}(k, t) = f_k \exp\{-[t/\tau(k)]\}^{\beta(k)}, \quad (19)$$

where  $f_k$  is called the nonergodicity parameter.<sup>9</sup> It should be noted that the idealized mode coupling theory predicts  $\beta(k)$  to depend only weakly on  $k$ . However, the available experiments and computer simulations on glass forming systems find the opposite. The wave vector dependence of the relaxation time  $\tau(k)$  and the parameter  $f(k)$  show nontrivial dependence on  $k$ . An important success of the mode coupling theory has been to provide accurate estimates of these quantities and to provide a physical explanation of the KWW form. Among these parameters  $\tau(k)$  shows the strongest  $k$ -dependence. In the intermediate wave vector region this can be approximated by<sup>9</sup>

$$\tau(k) = S(k)/(D_s k^2), \quad (20)$$

where  $D_s$  is the self-diffusion coefficient of the liquid. The nonexponential parameter  $\beta(k)$  also shows a nonmonotonic behavior, with a minimum near the peak of the structure factor. We assume a Lorentzian form for this function with a minimum value in the range of 0.3–0.5 and the maximum at  $k=0$  in the range 0.6–0.8—these are reasonable numbers. In this work we shall ignore the  $k$ -dependence of  $f_k$ . In addition, we shall now concentrate only on the mode-coupling contribution and ignore the phonon contribution which still gives an ultrafast component to nonpolar solvation, but less interesting in the supercooled liquid.

In Fig. 3 we present the results of our calculation of  $S(t)$  for a nonpolar solute in the supercooled region for two values in the high viscosity range. The value of the self-diffusion coefficient has been assumed to be given by the Stokes-Einstein relation. Here we have taken the reduced density of the liquid equal to 0.95 to allow for the formation of the structure at the molecular length scales. The sizes of the probe and the solvent molecules are the same. The stretched exponential parameter  $\beta(k)$  is assumed to vary between 0.4 and 0.7 with the minimum at  $k\sigma = 6.8$ . Note that the solvation in Fig. 3 is much slower than that observed in Fig. 2. In Fig. 4 we show the time dependence of the nonexponential parameter  $\beta$  [now for  $S(t)$ ]. This is evaluated by using

$$\beta(t) = \frac{\partial}{\partial \ln t} \{\ln[-\ln S(t)]\}. \quad (21)$$

For a true stretched exponential decay,  $\beta(t)$  should be independent of time. As shown in Fig. 4,  $S(t)$  shows a pronounced plateau at a value around 0.4. Thus, the solvation is described well by a stretched exponential form at long times. The initial fast decay in Fig. 3 originates from the large wave

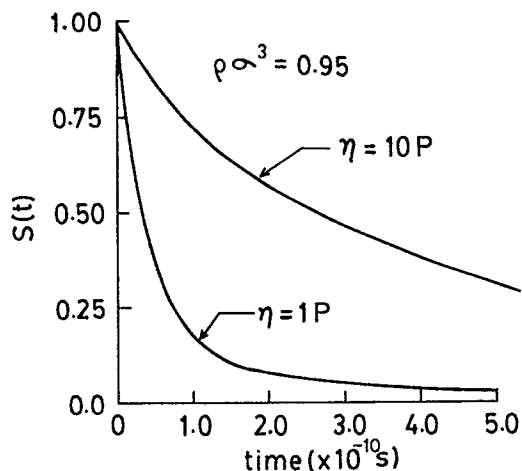


FIG. 3. The time dependence of the nonpolar solvation time correlation function,  $S(t)$ , in the supercooled liquid regime.  $S(t)$  is shown for two different values of the viscosity  $\eta$  (1 and 10 P) as shown directly on the curves. Here  $S(t)$  is evaluated using the Eq. (16) and  $F(k, t)$  is given by Eq. (19) of the text, respectively. The wave vector dependence of the non-exponentiality parameter  $\beta(k)$  of Eq. (19) is modeled by a Lorentzian with a minimum value of 0.4 at  $k\sigma=6.8$  and a maximum value of 0.7 at  $k\sigma=0$ . The other parameter values have been discussed in the text.

vector ( $K\sigma > 10$ ) contribution where relaxation is fast and which still makes a small but non-negligible contribution.

In Fig. 5 we show the probe size dependence of the nonpolar solvation dynamics, again including only the mode-coupling contribution. The relaxation is faster for the larger probe than that for the smaller one. This is because a probe with a size significantly larger than the size of the solvent molecules derives a much smaller contribution from the region where the relaxation is the slowest, that is, near  $k\sigma \cong 6.8$ , for a hard sphere model. The situation will clearly be rather different for more complex molecular liquids that are

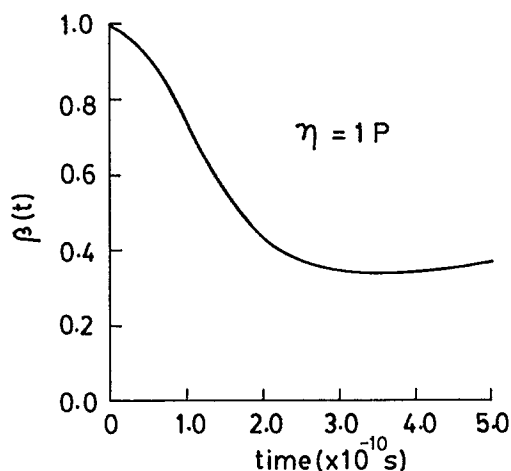


FIG. 4. The time dependence of the nonexponentiality parameter  $\beta(t)$  for the stretched exponential representation of  $S(t)$  in the supercooled liquid for the viscosity  $\eta=1$  P. The rest of the parameter values are the same as in Fig. 3.

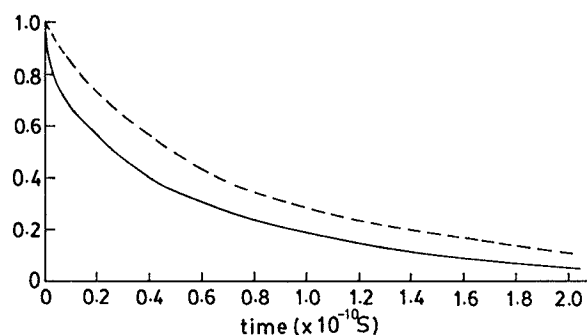


FIG. 5. The probe size dependence of the nonpolar solvation dynamics. Here solvation time correlation function  $S(t)$  is plotted for two values of the solute-solvent size ratio,  $r$ . The solid line is for  $r=2$  and the dashed line for  $r=0.5$ . The value of the viscosity is 1 P. The rest of the parameters have the same value as in Fig. 3.

studied experimentally. However, since the mode-coupling theory, the experiments and the simulations all suggest a nontrivial  $k$  dependence of the dynamic structure factor through the parameters  $\pi(k)$ ,  $f_k$ , and  $\beta(k)$ ,<sup>12</sup> we can expect the presence of a significant probe size dependence in nonpolar solvation dynamics.

#### IV. CONCLUSION

In this article we presented a simple molecular theory of nonpolar solvation dynamics. The main result of this study is an expression, given by Eq. (16), for the solvation time correlation function. This remarkably simple expression relates the nonpolar solvation dynamics directly to the dynamic structure factor and seem to provide at least a semiquantitative explanation of many of the interesting observations of Berg and co-workers. The theory predicts that at high temperatures nonpolar solvation is exponential-like with the relaxation dominated by the phonon and the viscous modes of the host solvent as the dynamic structure factor is described by the conventional Rayleigh-Brillouin spectrum.<sup>11</sup> However, the dynamics changes drastically at low temperatures. The theory predicts that here nonpolar solvation may become increasingly nonexponential as the temperature of the supercooled liquid is decreased towards the glass transition temperature. We have used the mode-coupling theory to relate the observed nonexponentiality to the slow density relaxations in the supercooled liquid. The theory further predicts that nonpolar solvation dynamics may be used as a probe of the length dependence of the relaxation phenomenon. Thus, it can provide a test of many of the predictions of the mode-coupling theory of glass transition. A quantitative evaluation of the solvation time correlation function in a particular liquid will require a detailed knowledge of the intermediate scattering function,  $F(k, t)$  over the whole wave vector and time domain. Therefore; we suggest that solvation experiments be carried out in such liquids where this information is available.<sup>12</sup>

The theory brings out significant differences between the polar and nonpolar solvation dynamics. While the long wavelength processes seem to dominate polar solvation, the molecular length scale processes are predicted to dominate



the nonpolar solvation dynamics. In addition, it is the translational rather than the orientational motion of the molecules that determine nonpolar solvation dynamics, in contrast to the polar solvation where the opposite is true. While polar solvation is ultrafast partly due to the small value of the longitudinal polarization relaxation time,<sup>1</sup> the nonpolar solvation is ultrafast because of the large value of the large wave number relaxation rates. It is of considerable importance to understand these differences in more detail.

There are several limitations of this work that should be rectified. The most prominent one perhaps is the neglect of the translational and the rotational motion of the solute. It is straightforward to include the translational motion, but it is nontrivial to treat the rotational motion of the solute. Another limitation is the assumption of the dynamic linear response of the host solvent to the probe solute. This can be important if there is a significant change in the nature of solute-solvent interactions in the ground and the excited electronic states of the solute probe. A third limitation of the present study is the use of a hard sphere model to obtain the required static correlation functions.<sup>10</sup> This can be rectified by directly using the experimental values of the required correlation functions along with the experimental dynamic structure factors. We hope that the present study will motivate further experimental and theoretical studies of nonpolar solvation dynamics.

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<sup>1</sup> See, for example, the papers in *Ultra-fast Chemical Reactions and Solvent Response*, edited by Y. Gauduel and P. J. Rossky (American Institute of Physics, New York, 1993).

<sup>2</sup> J. T. Fourkas and M. Berg, *J. Chem. Phys.* **98**, 7773 (1993).

<sup>3</sup> J. T. Fourkas, A. Benigno, and M. Berg, *J. Chem. Phys.* (in press).

<sup>4</sup> J. Yu, T. J. Kang, and M. Berg, *J. Chem. Phys.* **94**, 5787 (1991); T. J. Kang, J. Yu, and M. Berg, *Chem. Phys. Lett.* **174**, 476 (1991).

<sup>5</sup> T. Munakata, *J. Phys. Soc. Jpn.* **45**, 749 (1978).

<sup>6</sup> J. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 116 (1963).

<sup>7</sup> A. Chandra and B. Bagchi, *J. Phys. Chem.* **93**, 6996 (1989); *J. Chem. Phys.* **94**, 8367 (1991).

<sup>8</sup> B. Bagchi and A. Chandra, *Adv. Chem. Phys.* **80**, 1 (1991), and references therein.

<sup>9</sup> W. Gotze, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn Justin (Elsevier, New York, 1991).

<sup>10</sup> J. L. Lebowitz, *Phys. Rev.* **133**, 895 (1964).

<sup>11</sup> J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1986).

<sup>12</sup> See the papers in *Dynamics of Disordered Materials*, edited by D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira (Springer, Berlin, Heidelberg, 1989).