

# Solvation structure and the time-resolved Stokes shift in non-Debye solvents

Laurence E. Fried<sup>a)</sup> and Shaul Mukamel<sup>b)</sup>

Department of Chemistry, University of Rochester, Rochester, New York, 14627

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We develop a microscopic theory of the time-resolved Stokes shift of a chromophore in a polar solvent which incorporates both non-Debye dielectric relaxation and solvation shell structure. The present theory depends on the direct correlation function of the pure solvent, the measured frequency-dependent dielectric constant, and a microscopically derived translational diffusion parameter. We compare the predictions of the theory given here to a variety of experimental results on solvation in protic and aprotic solvents. Good agreement with experiment is found. Our theory compares favorably with the dynamical mean spherical approximation (MSA) theory of time-dependent solvation.

## I. INTRODUCTION

The time- and frequency-resolved fluorescence spectra of many chromophores show a time-dependent red shift which reflects the dynamics of solvent reorganization following the change in the intramolecular charge distribution upon optical excitation. Earlier experiments<sup>1</sup> measured the frequency shift (known as the Stokes shift) in solvents displaying a slow (500 ps and above) relaxation. The recent development of ultrafast laser technology and detection systems, however, has allowed the detailed observation of the fluorescence shift in the picosecond to femtosecond regime<sup>2-16</sup> for a wide range of common solvents. Femtosecond pump-probe techniques offer an even broader range of possibilities.<sup>17,18</sup> These experiments break new ground because they measure, with unprecedented detail, the time-resolved change in the interaction energy of the solute with the solvent. The red shift thus gives insight into a dynamical process of the greatest chemical significance: solvation.

Traditionally, theories of solvation dynamics have modeled the solvent as a dielectric continuum,<sup>19</sup> while the solute has been modeled as a cavity containing a charge or dipole. One of the principal predictions of dielectric continuum theory is that for a solvent characterized by a Debye dielectric relation, the energy of solvation relaxes exponentially with a time scale called the longitudinal time  $\tau_L$ . Experimental results have shown marked deviations from this prediction. Strongly nonexponential relaxation, and even exponential relaxation with a time scale very different from  $\tau_L$  have been observed.<sup>20</sup> Furthermore, recent simulations on solvation in water by Maroncelli and Fleming<sup>21</sup> point out the importance of shell structure in solvation. These results underline the need for a theory of solvation that takes into account the microscopic structure of the solvent. There has been previous theoretical work along these lines. Calef and Wolynes<sup>22</sup> proposed a generalized Smoluchowski equation for solvation dynamics. This equation took into account rotational degrees of freedom, and used the direct correlation function  $c(k)$  as an effective potential of interaction. Loring and Mukamel<sup>23</sup> studied solvation in a lattice of dipoles undergoing rotational diffusion, using density expansions.

Friedrich and Kivelson<sup>24</sup> have also pointed out the importance of molecular effects in solvation. Recently, Castner *et al.*<sup>25</sup> proposed an inhomogeneous dielectric continuum model that phenomenologically builds in molecular effects.

The most commonly applied microscopic theory of solvation, however, is the dynamical mean spherical approximation (MSA), which was proposed by Wolynes,<sup>26</sup> then extended by others.<sup>27-29</sup> Several other groups have compared the predictions of the dynamical MSA to experiments.<sup>10,20</sup> In general, the dynamical MSA provides qualitative agreement with experiment. The static mean spherical approximation of equilibrium statistical mechanics<sup>30</sup> is an approximate closure relation that allows the Ornstein-Zernicke equations to be solved for the direct correlation function  $c(k)$  and the pair distribution function  $h(k)$ . Wertheim has solved the dynamical MSA analytically for the simple model of dipolar hard spheres.<sup>31</sup> The dynamical MSA uses this approximation and the experimental dielectric function  $\epsilon(\omega)$  to incorporate solvation dynamics. Recently, Chandra and Bagchi<sup>32-36</sup> have revived the study of the generalized Smoluchowski equation, putting in translational degrees of freedom. Their equations apply to situations where the dielectric dispersion is of the Debye form. In addition, they assume a nonpolarized system, so that  $\epsilon_\infty = 1$ . We find below that both restrictions must be relaxed to obtain agreement with experiment.

In the present paper, we undertake three tasks. First, we derive a framework under which both *solvent structure* and *non-Debye dielectric relaxation* may be taken into account. By solvent structure, we refer to the fact that solvent molecules close to the solute may respond differently to the solute electric field than solvent molecules further away. In other words, shell structure is built in. Also, our theory is not restricted to a Debye dielectric dispersion, as the generalized Smoluchowski equation approach is. Non-Debye effects are incorporated in the solvent dielectric function  $\epsilon(\mathbf{k}, \omega)$  through its spatial ( $\mathbf{k}$ ) and spectral ( $\omega$ ) dispersion.

To derive this theory, we relate the energy of solvation to time-dependent equilibrium density correlation functions of the solvent. A generalized Langevin equation for these correlation functions is derived. In practice, it is very difficult to find the exact memory function. We introduce a simple approximation for the memory function that builds in

<sup>a)</sup> NSF Postdoctoral Fellow.

<sup>b)</sup> Camille and Henry Dreyfus Teacher-Scholar.

the effects of non-Debye dielectric dispersion. This gives us a theory of solvation that is parametrized by experimentally obtainable information, yet also can include molecular aspects of solvation, even in strongly non-Debye solvents.

Second, explicit equations are derived for the time-dependent energy of solvation in a non-Debye solvent. In these equations, the direct correlation function  $c(k)$  of the pure solvent enters, as well as the dielectric function  $\epsilon(\omega)$ . For the special case of a Debye solvent with  $\epsilon_\infty = 1$ , we recover the equation studied by Chandra and Bagachi.<sup>32-36</sup> We use the static mean spherical approximation for the direct correlation function  $c(k)$ . Thus, we have an *extendable* theory that uses virtually the same information as enters the dynamical MSA. The present theory, however, is not tied to the MSA or to the dipolar hard sphere model in any essential way. If experimental information or information from computer simulations is available on  $c(k)$ , it can be incorporated without trouble into the theory. This property is not shared by the dynamical MSA. The present theory can be easily applied to solute charge distributions other than a point charge or a point dipole.

Third, we compare our theory to a wide range of experimental results on the time-dependent Stokes shift in protic and aprotic solvents at various temperatures. The present theory shows qualitative agreement with experiment. It also generally gives better agreement with experiment than the dynamical MSA, especially in the case of alcohols. Non-Debye corrections are shown to be significant.

The rest of the paper is organized as follows: in Sec. II, we give a theoretical discussion that ends in the presentation and discussion of simple explicit formulas for the time-dependent energy of solvation. In Sec. III we apply these formulas to a wide range of experimental observations. Concluding remarks are made in Sec. IV. A detailed derivation of our theory is given in Appendix A.

## II. TIME-DEPENDENT SOLVATION

In this section we present a new theory for the time-dependent solvation energy  $E_S(t)$  that depends on the direct correlation function of the pure solvent and on the dielectric function  $\epsilon(\omega)$ . In the spirit of the Born theory of solvation,<sup>37</sup> we consider a liquid with a single tagged particle (the solute) at thermal equilibrium at  $t = 0$ . We then change the solute charge distribution, creating a specified time-dependent displacement field  $\mathbf{D}(\mathbf{r}, t)$  in the medium. This external displacement field, in turn, induces a polarization field in the medium  $\mathbf{P}(\mathbf{r}, t)$ . The time-dependent Born solvation energy  $E_S(t)$  can be related to the solvent polarization  $\mathbf{P}(\mathbf{r}, t)$  by

$$E_S(t) = - \int_{-\infty}^{\infty} d\mathbf{r} \mathbf{P}(\mathbf{r}, t) \cdot \mathbf{D}(\mathbf{r}, t). \quad (1)$$

It is useful to introduce the dimensionless correlation function of the solvation energy  $E_S(t)$ ,

$$S(t) = \frac{E_S(t) - E_S(\infty)}{E_S(0) - E_S(\infty)}. \quad (2)$$

$S(t)$  is directly measured in a time-dependent Stokes shift experiment. The same function also appears in theories<sup>38</sup> and experimental studies<sup>39</sup> of electron transfer processes.

We consider here only the linear part of the solvent response to the solute field  $\mathbf{D}$ , and neglect higher order (dielectric saturation) effects. Recent simulations by Maroncelli and Fleming<sup>21</sup> have shown that linear response theory accounts for most of the solvation behavior in ionic solvation in water. Using linear response theory, we introduce the polarizability tensor  $\alpha(\mathbf{r}, \mathbf{r}', t)$  such that

$$\mathbf{P}(\mathbf{r}, t) = \int_{-\infty}^{\infty} d\mathbf{r}' \int_0^t dt' \alpha(\mathbf{r}, \mathbf{r}', t - t') \cdot \mathbf{D}(\mathbf{r}', t'). \quad (3)$$

All microscopic information regarding the time-dependent solvation process is contained in the polarizability  $\alpha$ . It is convenient to transform the polarizability into wave vector-Laplace ( $\mathbf{k}, s$ ) space. We define, for example,

$$\mathbf{P}(\mathbf{k}, s) = \int_{-\infty}^{\infty} d\mathbf{r} \int_0^{\infty} dt e^{i\mathbf{k} \cdot \mathbf{r} - st} \mathbf{P}(\mathbf{r}, t). \quad (4)$$

This gives us

$$\mathbf{P}(\mathbf{k}, s) = \int_{-\infty}^{\infty} d\mathbf{k}' \alpha(\mathbf{k}, \mathbf{k}', s) \cdot \mathbf{D}(\mathbf{k}', s). \quad (5)$$

Let us define the part of the solvent polarizability coming from nuclear degrees of freedom as  $\alpha'$ :

$$\alpha(\mathbf{k}, \mathbf{k}', s) = \alpha'(\mathbf{k}, \mathbf{k}', s) + \alpha_\infty(\mathbf{k}, \mathbf{k}'), \quad (6)$$

where  $\alpha_\infty(\mathbf{k}, \mathbf{k}')$  represents the contribution of electronic (high frequency) degrees of freedom to the solvent polarizability. The separation of  $\alpha(k, s)$  into nuclear and electronic contributions has been reviewed by Madden and Kivelson<sup>40</sup> [see Eq. (3.21) in their paper]. This separation is entirely analogous to parametrizing electronic effects in the dielectric function by  $\epsilon_\infty$ .<sup>41</sup> As Madden and Kivelson discuss, the nuclear contribution to the macroscopic polarizability may be viewed as coming from an effective permanent dipole moment. Thus, we use a polar but nonpolarizable model of the solvent molecules to find  $\alpha'$ .

Since  $\alpha_\infty$  leads to an extremely fast relaxation of the polarization  $\mathbf{P}$ , we need consider only the nuclear part of the solvent polarizability [ $\alpha'(k, s)$ ]. The solvent polarizability can be decomposed into transverse and longitudinal parts:<sup>23</sup>

$$\alpha(\mathbf{k}, s) = \hat{\mathbf{k}} \hat{\mathbf{k}} \alpha_L(k, s) + (\hat{\mathbf{u}}\hat{\mathbf{u}} + \hat{\mathbf{v}}\hat{\mathbf{v}}) \alpha_T(k, s), \quad (7)$$

where  $\hat{\mathbf{u}}$  and  $\hat{\mathbf{v}}$  are unit vectors perpendicular to  $\hat{\mathbf{k}}$ .  $\alpha_L$  and  $\alpha_T$  are called the longitudinal and transverse parts of the polarizability, respectively.

The solvent polarizability can be related to the orientation/position density of the solvent  $\rho(\mathbf{r}, \Omega, t)$ :

$$\rho(\mathbf{r}, \Omega) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\Omega - \Omega_i). \quad (8)$$

In Appendix A, we derive approximate equations of motion for  $\rho(\mathbf{r}, \Omega)$  based on the generalized Langevin equation for density fluctuations. We consider dipolar, nonpolarizable solvent molecules of diameter  $\sigma$  whose orientation is described by their dipole moment vector  $\boldsymbol{\mu}$ . The molecules are assumed to have a single nonzero moment of inertia  $I$ . Our final result for the longitudinal part of the polarizability is

$$\alpha'_L(k,s) = \frac{1}{4\pi} \left[ \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right] \left\{ \frac{1 - \rho_0 c_L(k)}{1 - \rho_0 c_L(0)} - \frac{1}{1 + p'(k\sigma)^2} \frac{\epsilon_\infty [\epsilon(s) - \epsilon_0]}{\epsilon_0 [\epsilon(s) - \epsilon_\infty]} \right\}^{-1}, \quad (9)$$

where we use the notation  $c_L(k) \equiv c(k, l_1 = 1 = l_2 = 1, m = 0)$  for the direct correlation function  $c$  in the  $\mathbf{k}$  frame.<sup>30</sup>  $\epsilon_0 \equiv \epsilon(k = 0, s = 0)$ , and  $\epsilon_\infty \equiv \epsilon(k = 0, s = \infty)$ . Also, we call

$$p' = I/2M\sigma^2 \quad (10)$$

the translation diffusion parameter,  $\sigma$  is the solvent diameter, and  $\beta = 1/k_B T$ .  $p'$  corresponds to the translational diffusion parameter used by Chandra and Bagchi,<sup>36</sup> and Van der Zwan and Hynes;<sup>42</sup> in their work, however,  $p' = D_T/2D_R\sigma^2$ , where  $D_T$  and  $D_R$  are measured rotational and translational diffusion coefficients,  $\rho_0 = \rho/4\pi$ , where  $\rho$  is the number density of the solvent.

We find for the transverse polarizability that

$$\alpha'_T(k,s) = \frac{\epsilon_0 - \epsilon_\infty}{4\pi} \left[ \frac{1 + \rho_0 c_T(k)}{1 + \rho_0 c_T(0)} - \frac{1}{1 + p'(k\sigma)^2} \frac{\epsilon(s) - \epsilon_0}{\epsilon(s) - \epsilon_\infty} \right]^{-1}, \quad (11)$$

and  $c_T$  is a shorthand notation for  $c(k, 1, 1, 1)$ . Equations (9) and (11) constitute a closed-form result for the  $k$  and  $s$  dependent polarizability of the pure solvent. Note that the dielectric continuum result is trivially recovered in Eqs. (9) and (11) by setting  $k = 0$ . Using (1), we obtain an explicit result for the energy of solvation of a suddenly created charge distribution:

$$E_S(s) = \frac{-1}{8\pi^3 s} \int_{-\infty}^{\infty} d\mathbf{k} \alpha'_L(k,s) |D_L(\mathbf{k})|^2 + \alpha'_T(k,s) |D_T(\mathbf{k})|^2. \quad (12)$$

Equations (9) and (11) also can be viewed as a formula for the  $k$  and  $s$  dependent dielectric function, through the relations

$$\frac{1}{\epsilon_L(k,s)} - \frac{1}{\epsilon_L(k,\infty)} = -4\pi\alpha'_L, \quad (13)$$

$$\epsilon_T(k,s) - \epsilon_T(k,\infty) = 4\pi\alpha'_T. \quad (14)$$

These are useful relationships, since  $\epsilon(k,s)$  appears in theories of optical line shapes and electron transfer reactions.<sup>43</sup>

Before proceeding to apply these formulas, let us critically review the approximations that went into their derivation.

**Separation of  $\alpha(k,s)$  into electronic and nuclear contributions.** The picosecond time scales of a typical solvation experiment indicate that electronic degrees of freedom are not important in solvation. To take advantage of this, we divide the polarizability into contributions from nuclear and electronic degrees of freedom,<sup>40</sup> then use a *permanent* dipole model for the nuclear degrees of freedom. Thus, we consider here only contributions to solvation coming from nuclear motion. Our theoretical treatment is completely consistent

with recent simulations of solvation in water,<sup>21</sup> which also used nonpolarizable models.

**Linear solvent.** We have assumed linear solvent molecules, so that their orientation may be fully described by the orientation of molecular dipole moment. It is reasonable to assume that dielectric relaxation does not depend strongly on degrees of freedom that do not directly effect the orientation of the molecular dipole moment.

**Stationary solute.** We assume that the solute molecule is sufficiently massive that its motion may be ignored. This approximation is justified by the large molecular weight of typical dye molecules used in Stokes shift experiments, compared with the molecular weight of typical solvents.

**Linear response.** In casting our results in terms of the polarizability  $\alpha$ , we have neglected any nonlinear response to the solute field  $\mathbf{D}$ . The present theory should work best for solutes with small dipole moments. This could be a reason for some concern, since time-dependent Stokes shift experiments are often carried out with "giant dipole" (about 20 D) dye molecules. Nonetheless, recent simulations on solvation in water by Maroncelli and Fleming<sup>21</sup> suggest that linear response can account for many of the qualitative features of solvation in realistic systems.

**Cutoff fields.** We have assumed that the polarizability of the solute-solute system is given by the pure solvent polarizability with the  $\mathbf{D}$  field set to zero inside the solute. This is the simplest way to treat finite solute size. Chandra and Bagchi<sup>32-36</sup> have used this approximation. The cutoff field approximation ignores specific solute/solvent interactions, and assumes that the equilibrium structure of the solvent in the neighborhood of the solute is the same as the bulk equilibrium structure of the solvent.

**Factorization approximation.** We have built non-Debye dielectric relaxation into the theory by writing the memory kernel for density fluctuations function as a function of frequency times a function of wave vector. The clearest way to understand the factorization is by analogy with Padé approximation. In Padé approximation, if the limiting behavior of a function as  $x \rightarrow \infty$  is known, that behavior is built into approximants that reproduce the Taylor expansion about  $x = 0$ . In our case, the continuum ( $k = 0$ ) behavior is known from dielectric experiments. Therefore, we will use a relaxation function  $r(s)$  to explicitly build correct continuum behavior into our theory through the factorization of the memory kernel. Just as Padé approximants can be systematically improved, so can the simple factorization presented here. This is discussed in detail in Appendix C. Physically, the factorization says that the rate of relaxation of density fluctuations depends on  $k$ , but the functional form of the relaxation does not depend on  $k$ . Since observable quantities  $[S(t)]$  involve integrals over  $k$ , we expect that the overall rate of relaxation as a function of  $k$  is more important than the particular functional form of relaxation.

**Angular decoupling.** We have assumed that the memory kernel for density fluctuations does not couple different values of  $l$ . This approximation is not essential, and can easily be relaxed. If the direct correlation function is treated within the mean spherical approximation, the angular decoupling approximation is satisfied. It may be important, however, to

include the coupling between various  $l$  values in hydrogen-bonded solvents, where angular correlations are expected to be very strong. Chandra and Bagchi have used the angular decoupling approximation.<sup>32-36</sup>

Although this set of approximations may not be justified for all solute/solvent combinations, we believe that the present treatment gives a simple analytic treatment of the polarizability that may be very useful as a point of departure for more exact treatments. Furthermore, our discussion builds in many important physical features of solvation. The molecular nature of solvation (shell structure, etc.) enters through the direct correlation function  $c$ . The solute charge distribution can be built in through the applied field  $\mathbf{D}(\mathbf{k})$ . The present theory is not limited to any particular approximation for the direct correlation function, such as the mean spherical approximation. This is an important point, since it is well known<sup>30</sup> that many features of highly polar solvents (i.e., reduced dipole moment greater than 1) are poorly treated by the MSA. We also believe it is important that dynamical effects enter through the dielectric function  $\epsilon(\omega)$ . Recent simulations of solvation in water<sup>21</sup> imply that concerted motions of the solvent molecule may be important. These effects are approximately accounted for in the present treatment. Also, the theoretical program set forth here can be systematically improved (see Appendix C). The improvements outlined in Appendix C require the knowledge of higher order distribution functions  $g^{(n)}$ . These distribution functions could be obtained by computer simulation, a quasianalytical theory of the polar fluid, or through a crude superposition approximation. In the next section, we compare the results of the simple theory given by Eq. (9) to time-dependent Stokes shift experiments in polar solvents.

### III. COMPARISON TO TIME-RESOLVED STOKES SHIFT MEASUREMENTS

In a time- and frequency-resolved fluorescence measurement, a dilute solution containing a chromophore is excited by a short pulse. The subsequent spectrally dispersed fluorescence is then recorded as a function of delay time. At very short times the fluorescence narrows due to the selectivity of the excitation.<sup>44</sup> As time evolves, the emission broadens and undergoes a red shift (the Stokes shift). These are signatures of the solvent reorganization following the sudden change in the charge distribution of the chromophore upon optical excitation.

A detailed analysis of the fluorescence line shape requires the introduction of the solute vibronic structure,<sup>44</sup> and will not be done here. Also, we assume an "ideal solute" molecule that does not have strong interactions (such as hydrogen bonding) with the solvent, and does not have charge transfer states.

The frequency shift can be conveniently expressed in terms of a normalized correlation function  $C(t)$  which decays from 1 to 0 as time increases:

$$C(t) = \frac{\omega(t) - \omega(\infty)}{\omega(0) - \omega(\infty)}, \quad (15)$$

where  $\omega(t)$  is the peak of the fluorescence emission at time  $t$ . Theories of fluorescence line shapes of solvated molecules<sup>38</sup>

predict that this correlation function is the same as the correlation function  $S(t)$  of the solvation energy  $E_S(t)$ , provided the field  $\mathbf{D}(\mathbf{r},t)$  is taken to be equal to the difference of the field created by the solute in the excited state and the ground state. It is this difference that the solvent polarization responds to. In addition, we assume that the external field is switched on instantaneously, so that

$$\mathbf{D}(\mathbf{k},s) = \frac{\mathbf{D}(\mathbf{k})}{s}. \quad (16)$$

The entire time-dependent line shape can also be calculated using  $S(t)$ .

In this section we compare theoretical results for  $E_S(t)$  to recent experiments. Before beginning this comparison, however, we will outline the numerical procedures that went into obtaining the results, then consider several predictions of the theory. The applied field  $\mathbf{D}(\mathbf{r},t)$  is equal to

$$\mathbf{D}(\mathbf{r},t) = \begin{cases} 0 & t < 0 \\ \hat{\mathbf{r}}/|\mathbf{r}|^2 & t \geq 0, \quad r \geq r_c \\ 0 & t \geq 0, \quad r < r_c \end{cases}. \quad (17)$$

As discussed in Appendix A, using a cutoff field is equivalent to assuming that the solute does not affect the structure of the bulk fluid, other than excluding volume. The cutoff field approximation has been used previously in treatments of solvation.<sup>32-36</sup> Since the applied field is longitudinal, it is sufficient to consider only the longitudinal part of the polarizability  $\alpha_L$ . A cutoff dipolar field, of the form of Eq. (17) would contain a transverse component as well.

The energy of solvation at a particular value of Laplace variable  $s$  is given by

$$E_S(s) = \frac{-1}{2\pi^2 s} \int_0^\infty dk k^2 \alpha'_L(k,s) |D_L(k)|^2, \quad (18)$$

where

$$D_L(k) = \frac{\pi/2 - \text{Si}(kr_c)}{k} \quad (19)$$

and Si denotes the standard sine integral.

The determination of the time-dependent energy of solvation thus requires the following procedure: the longitudinal polarizability  $\alpha_L(k,s)$  is evaluated using the formula given in Eq. (9). A numerical integral over  $k$  values [Eq. (18)] is then performed, followed by an inverse Laplace transform. We have used the trapezoid rule for the integral over  $k$ , followed by an inverse Laplace transform with the IMSL library function DINLAP, which implements the algorithm given by Crump.<sup>45</sup> In the following calculations the integral over  $k$  used 8192 points with a maximum value of  $k$  equal to  $16\pi/\sigma$ , where  $\sigma$  is the solvent diameter.

Let us review at this point the information necessary for the current solvation theory. In order to calculate the correlation function  $S(t)$ , we need:

*The applied field  $D(k)$ .* In the present calculation we consider the response to a cutoff point charge suddenly introduced on the solute molecule. The only parameter needed to determine the applied field is thus the solute radius  $r_c$ . In the calculations below, the solute radius  $r_c$  (and solvent radius  $\sigma$ ) was found by converting the van der Waals molecular volume<sup>46,47</sup> to an effective spherical radius.

The longitudinal part of the direct correlation function  $c_L(k)$ . This is determined within the MSA by the static dielectric constant  $\epsilon_0$  of the solvent. Explicit equations for  $c_L(k)$  are given in Appendix D.

The dielectric function  $\epsilon(s)$  As mentioned in Sec. II, the experimental dielectric function is used to incorporate non-Debye behavior into the theory.

The ratio of the solvent mass to its moment of inertia. This ratio can be expressed by the dimensionless parameter  $p' = I/2M\sigma^2$ , which corresponds to the translational diffusion parameter  $p' = D_T/2D_R\sigma^2$  used by Bagchi<sup>33</sup> and Hynes.<sup>42</sup> Since all the solvent molecules considered here are nonlinear, we take the moment of inertia  $I$  to be the average of the two largest principal moments of the solvent molecule in its equilibrium geometry, as determined by the MM2-M optimization of the program MODEL.<sup>48</sup>

The number density of the solvent  $\rho$ . In Appendix D we show that once the static dielectric constant  $\epsilon_0$  is fixed, results are independent of  $\rho$  within the MSA.

We next consider the general predictions of the present theory using the above ingredients. According to the dielectric continuum model, the solvation energy of a point charge immersed in a solvent with a Debye dispersion relation

$$\epsilon(s) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + s\tau_D} \quad (20)$$

will relax exponentially in time, with a time scale  $\tau_L = \tau_D\epsilon_\infty/\epsilon_0$ . Figure 1 shows a plot of  $\ln S(t)$  vs  $t/\tau_D$  for a model solvent with  $2r_c = \sigma$  for a range of values of the translational diffusion parameters  $p'$  ranging from 0.0 to 0.5. The parameters used in Figs. 1–4 are given in Table I. The decay is strikingly nonexponential for all but the largest values of  $p'$ . This is in accord with experiment: it is now well known that Debye solvents can and often do yield  $S(t)$  functions that show a nonexponential decay. Second, we note that as the translational diffusion parameter  $p'$  is increased, the observed decay becomes more nearly exponential, with a time scale approaching  $\tau_L$ . The physical interpretation of this ef-

TABLE I. Parameters used in the calculations of Figs. 1–4.

Figure	Form of $\epsilon(s)$	Params for $\epsilon(s)$	$d^{**}$	$p'$
1	Debye	$\epsilon_0 = 20.0$ $\epsilon_\infty = 2.0$ $\tau_D = 1.0$ ps	1.0	0.0...0.5
2	Cole–Davidson	$\epsilon_0 = 20.0$ $\epsilon_\infty = 2.0$ $\tau_0 = 1.0$ ps $\beta = 0.75$	1.0	0.0...0.5
3	Debye	$\epsilon_0 = 20.0$ $\epsilon_\infty = 2.0$ $\tau_D = 1.0$ ps	0.5...4.0	0.1
4	Cole–Davidson	$\epsilon_0 = 20.0$ $\epsilon_\infty = 2.0$ $\tau_0 = 1.0$ ps $\beta = 0.75$	0.5...4.0	0.1

\*  $d^{**} \equiv 2r_c/\sigma$ .

fect is that rapid translation “smears out” solvation shell structure, leading to dielectric continuum results. Chandra and Bagchi<sup>32–36</sup> have already noted this effect in the application of a generalized Smoluchowski equation to solvation. Their theory is equivalent to the present theory for a Debye solvent with  $\epsilon_\infty = 1$ . Finally, Fig. 1 shows that translational diffusion can have a substantial role in accelerating solvation: a modest increase in the translational diffusion parameter can dramatically affect the rate of solvation, especially in the neighborhood of  $p' = 0$ .

Solvation in non-Debye solvents also shows a strong dependence on translational diffusion. The Cole–Davidson functional form is commonly used to represent  $\epsilon(\omega)$  for non-Debye solvents. It is given by

$$\epsilon(s) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + s\tau_0)^\beta} \quad (21)$$

In Fig. 2 we show  $S(t)$  for various values of  $p'$  when  $\beta = 0.75$ , other parameter values are given in Table I.  $S(t)$  for a Cole–Davidson solvent shows a greater range of time

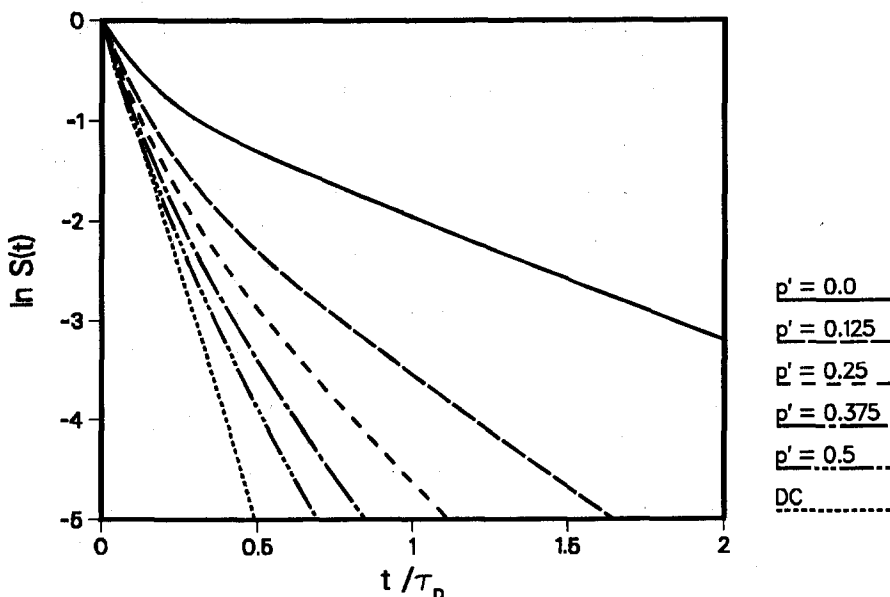


FIG. 1.  $\ln S(t)$  is shown as a function of  $t$ , for a Debye solvent. The present theory is used with various values of the translational diffusion parameter  $p'$ . Also shown are the results of dielectric continuum (DC) theory. The full set of parameters used in the calculation are given in Table I.

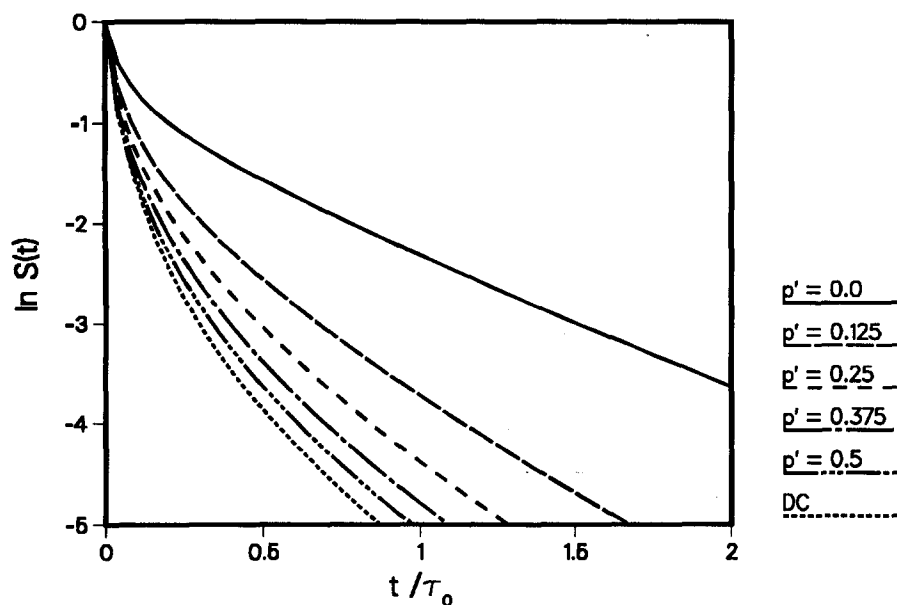


FIG. 2.  $\ln S(t)$  is shown for a Cole–Davidson solvent with  $\beta = 0.75$ . As in Fig. 1, various values of the translational diffusion parameter are used. Also shown are the results of dielectric continuum (DC) theory.

scales than in the Debye solvent; the initial relaxation is faster, while the relaxation at longer times is slower. As in the case of a Debye solvent, increased translational diffusion leads to a faster decay of  $S(t)$ . Unlike a Debye solvent, however, the decay is nonexponential even when  $p'$  is large. In the large  $p'$  limit, dielectric continuum behavior is reproduced as shell structure is smeared out by rapid translation.

Another important parameter influencing  $S(t)$  is the relative solute/solvent size. In Fig. 3 we plot  $S(t)$  for a Debye solvent at various values of the relative solute diameter  $d^* = 2r_c/\sigma$ . Other parameters used in the calculation are given in Table I. As the relative solute size is increased, the rate of solvation increases then decreases. In the limit of large solute size  $S(t)$  decays with a single time scale given by  $\tau_L$ . This is expected; when the solute becomes sufficiently large the solvent is well approximated by a continuum, and the prediction of continuum theory is recovered. This behav-

ior can be understood analytically. As the solute radius  $r_c$  is increased, the applied field  $\mathbf{D}(\mathbf{k})$  selects only the  $k = 0$  part of  $\alpha_L$ , i.e., we have

$$\lim_{r_c \rightarrow \infty} \mathbf{D}(k) \propto \delta(kr_c). \quad (22)$$

By construction, however, the present theory for  $\alpha'_L$  recovers continuum theory in the limit of  $k \rightarrow 0$ . This may be explicitly verified by inspection of Eq. (9).

Figure 4 shows the effect of solute size on a Cole–Davidson solvent with  $\beta = 0.75$ . The rate of solvation is seen to increase, then decrease, as the relative solute size  $d^*$  is increased from 0.5 to 4.0, which is the same pattern shown in Fig. 3. At the larger values of  $d^*$ , however, the decay is not exponential. This is because continuum dielectric theory does not predict exponential decay of  $S(t)$  for non-Debye solvents.

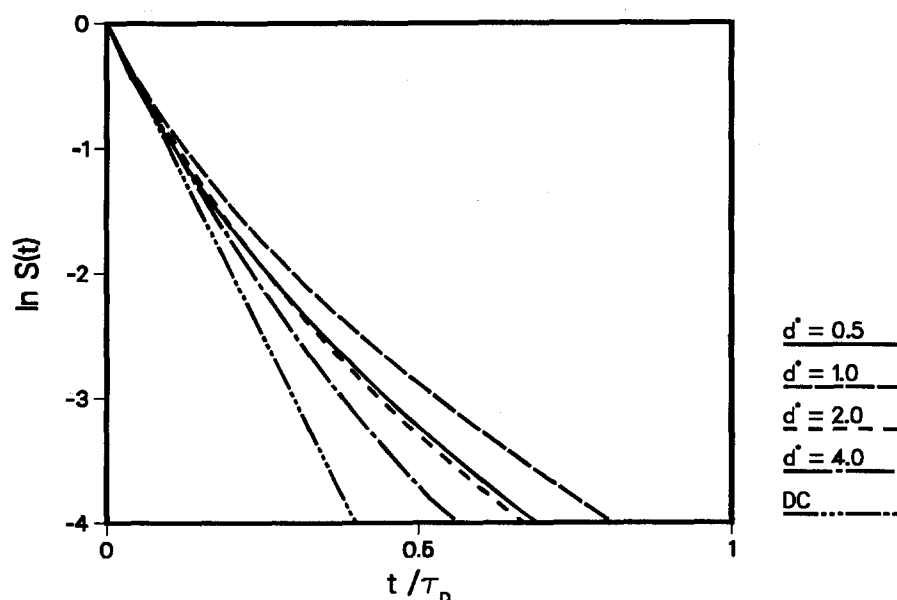


FIG. 3.  $\ln S(t)$  is shown for a Debye solvent under the present theory and dielectric continuum theory for various value of the solute/solvent diameter ratio  $d^*$ .

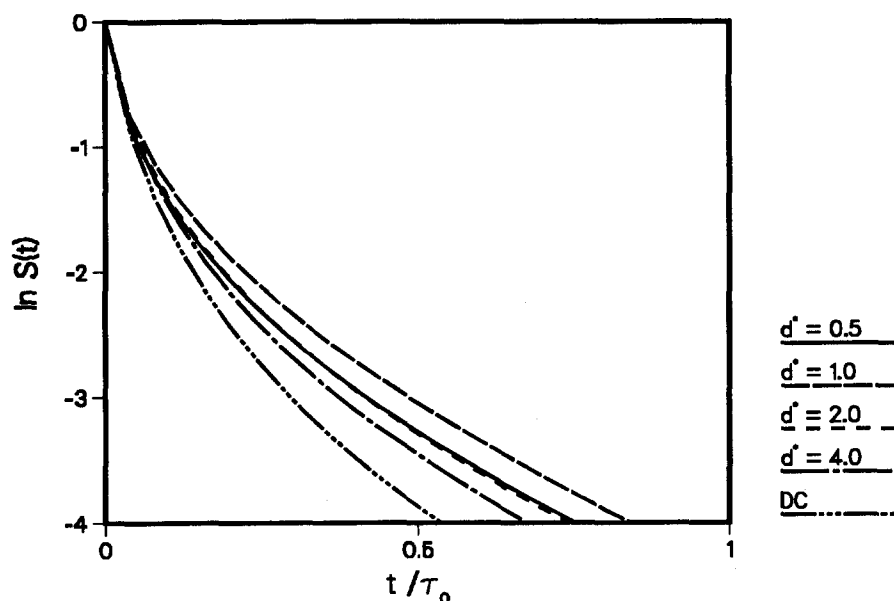


FIG. 4.  $\ln S(t)$  is shown for a Cole-Davidson solvent with  $\beta = 0.75$ . As in Fig. 3, various values of the solute/solvent diameter ratio  $d^*$  are used. Also shown are the results of a dielectric continuum (DC) calculation.

### A. Protic solvents

We next apply the present theory to the time-dependent Stokes shift in alcohols and water. Dielectric data for the calculations that follow is compiled in Refs. 4, 10, and 21. A convenient basis of comparison with experiment is the mean relaxation time  $\langle \tau \rangle$ , given by

$$\langle \tau \rangle = \int_0^{\infty} S(t) dt. \quad (23)$$

Table II gives mean relaxation time  $\langle \tau \rangle$  for alcohols with dielectric dispersion that is best (within experimental uncertainty) fit to a Debye form. All of the alcohols in Table II give an experimental dimensionless solvation time  $\tau_E = \langle \tau \rangle / \tau_L$  close to 1; in other words, corrections to the dielectric continuum model prediction for the mean solvation time are small. Bagchi and Chandra have rationalized this result within the framework of a generalized Smoluchowski equation by pointing out that the measured translational diffusion constant leads to  $S(t)$  decay that is nearly exponential. They have not, however, made direct comparison with experimental results.

Also given in Table II, are mean relaxation times predicted by the present theory and the dynamical MSA applied to ionic solvation. In Table II and below, the mean solvation times for the MSA were estimated by integrating published graphs of  $S(t)$  or  $\ln S(t)$  when numerical data were unavail-

able. Both the dynamical MSA and the present theory give relaxation times that are too long for all solvents considered. The present theory, however, is closer to the experimental values than the dynamical MSA for all solvents considered. Sometimes (e.g., EtOH) the correction offered by the present theory can be considered.

In Table III we consider mean relaxation times for methanol at room temperature and propanol at various temperatures. For these solvents, sufficient dielectric data exists to give a non-Debye fit. In both cases, the dielectric function is represented as a sum of exponentials. Following the form of Castner *et al.*<sup>4</sup> we have

$$\epsilon(s) = \epsilon_{\infty} + \sum_{i=1}^n \frac{\epsilon_0^{(i)} - \epsilon_{\infty}^{(i)}}{1 + s\tau_i}. \quad (24)$$

For propanol,  $n = 3$ , while for methanol  $n = 2$ . The solvation times in Table III have been divided by  $\tau^* = \tau_1 \epsilon_{\infty}^{(1)} / \epsilon_0^{(1)}$ , which is a rough indicator of the solvation time. The relaxation times predicted by the present theory are in very good agreement with the experimental relaxation times for propanol. Moreover, the general trend of increasing reduced solvation time with decreasing temperature is qualitatively reproduced by the present theory.

Figure 5 shows a graph of experimental results and results of the dynamical MSA (for ionic solvation; transcribed from Ref. 20), along with the predictions of the present theo-

TABLE II. Relaxation times for alcohols with a Debye  $\epsilon(s)$ .

Solvent	$T(K)$	$\epsilon_0$	$\epsilon_{\infty}$	$\tau_D$ (ps)	$d^*$	$p'$	$\tau_E^a / \tau_L$	$\tau_{MSA}^b / \tau_L$	$\tau^c / \tau_L$
EtOH	253	32.4	4.86	643	1.69	0.031	1.2	1.9	1.4
2-PrOH	253	26.4	3.70	3050	1.54	0.027	1.1	2.0	1.8
n-PrOH	251	27.8	3.94	2140	1.54	0.044	1.0	2.0	1.6
n-BuOH	253	23.7	3.65	3220	1.43	0.060	1.0	1.8	1.8

<sup>a</sup> Experimental solvation times of Ref. 20.

<sup>b</sup> MSA prediction for ionic solvation; taken from Ref. 20.

<sup>c</sup> Prediction of the present theory.

TABLE III. Relaxation times for hydrogenic solvents with a non-Debye  $\epsilon(s)$ .

Solvent	T(K)	$a_1^a$	$a_2$	$a_3$	$\epsilon_\infty$	$\tau_1$ (ps)	$\tau_2$	$\tau_3$	$d^*$	$p'$	$\tau_E^b/\tau^*$	$\tau_{MSA}^c/\tau^*$	$\tau^d/\tau^*$
n-PrOH	295	17.34	0.63	0.83	2.20	457	19.5	2.2	1.54	0.044	0.8	1.6	0.8
	273	20.36	0.73	0.83	2.23	891	24.6	2.8			0.9	1.7	0.8
	251	23.86	0.84	0.82	2.28	2089	35.5	4.1			1.0	1.9	0.9
	232	27.35	0.96	0.82	2.32	5129	57.7	6.5			1.0	2.1	0.9
	221	29.63	1.04	0.81	2.35	9550	83.2	9.3			1.1	2.2	0.9
MeOH	298	27.0	1.79	0.0	3.68	51.02	3.29		1.77	0.019 0.77 <sup>f</sup>	1.1	1.5	1.9
Water <sup>e</sup>	298	$\epsilon_0$	$\epsilon_\infty$	$\tau_0$	$\alpha$				2.9	0.006 0.28 <sup>f</sup>	1.9	2.3	3.5
		79.2	4.2	8.72 ps	0.013								

<sup>a</sup> We define  $a_n = \epsilon_0^{(n)} - \epsilon_\infty^{(n)}$ .

<sup>b</sup> Experimental solvation time of Refs. 10 and 20 divided by  $\tau^* = \tau_1 \epsilon_\infty^{(1)} / \epsilon_0^{(1)}$ .

<sup>c</sup> Ionic solvation time predicted by the dynamical MSA, taken from Refs. 10 and 21.

<sup>d</sup> Ionic solvation time predicted by the present theory.

<sup>e</sup> A Cole-Cole dielectric function was used. Experimental results were taken from Ref. 8.  $\tau^* = \epsilon_\infty \tau_0 / \epsilon_0$ .

<sup>f</sup> The translational diffusion parameter  $p'$  was determined by self-diffusion measurements.

ry for *n*-propanol at 251 K. The dynamical MSA predicts a decay that is significantly slower and more nonexponential (i.e., more curved on a log plot) than the experimental observations. The present theory, when used with a Debye  $\epsilon(\omega)$  gives a decay somewhat faster and more exponential than that of the dynamical MSA. When used with a non-Debye  $\epsilon$ , however, the present theory gives very good agreement with experiment, the principal disagreement being an initial decay that is more rapid than is observed experimentally. Table III also gives relaxation times for methanol at room temperature. Both the dynamical MSA and the present theory give relaxation times that are too slow, but in this case the mean time predicted by the MSA is in somewhat better agreement with experiment than the present theory. It is perhaps significant that methanol has an exceptionally low  $p'$  value.

In Table III we also give a mean solvation time for methanol based on using an experimentally determined  $p'$

value. We do so by defining  $p'$  in terms of measured rotational and translational diffusion constants

$$p' = D_T / 2D_R \sigma^2. \quad (25)$$

$D_T$  is then taken from the measured self-diffusion constant of methanol,<sup>49</sup> whereas  $D_R$  is estimated as  $\tau_1/2$ . This leads to a predicted solvation time that is faster than the measured value.

The predicted mean solvation time for water, also shown in Table III, is considerably slower than the experimental value. Since  $p'$  is very small for water, it is reasonable to surmise that solvents with low reduced moments of inertia are poorly treated by the present calculation. In the case of water, using an experimentally determined  $p'$ <sup>49</sup> leads to a solvation time that is faster than the experimental time. A more rigorous extension of the present theory would require calculating additional levels in the Mori hierarchy, thereby

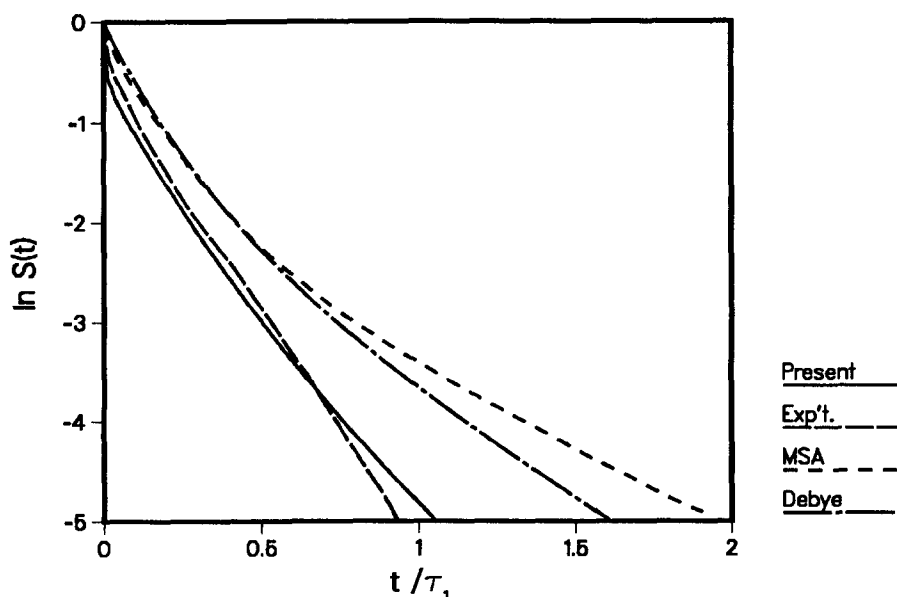


FIG. 5. In  $S(t)$  is shown for *n*-propanol at 251 K. Illustrated are experimental results (Ref. 20), results of the MSA with a Debye  $\epsilon(s)$  (Ref. 20), the result of the present theory with a non-Debye  $\epsilon(s)$ , and the results of the present theory with a Debye  $\epsilon(s)$  (labeled Debye).



treating correlated motions of the solvent molecules more exactly. This idea is explored further in Appendix C.

## B. Nonhydrogenic polar solvents

We now apply the present theory to propylene carbonate and propionitrile. Table IV gives a summary of our results. Experimental and theoretical results are given for propylene carbonate at several temperatures ranging from 221 to 298 K. With the sole exception of propylene carbonate at room temperature, the experimental reduced solvation times are significantly greater than 1. This means that solvation occurs more slowly than a simple continuum theory with a Debye  $\epsilon$  would predict. A wide range of experimental relaxation times are observed (from 2 to 346 ps). For the calculations at temperatures less than 298 K, a Debye form for  $\epsilon(s)$  was used. For all the "cold" experiments, the present theory shows better agreement with experiment than the dynamical MSA. Both the dynamical MSA and the present theory, however, give relaxation times that are too fast. Furthermore, both the dynamical MSA and the present theory do not show the anomalously slow relaxation observed at 221 K. We show the log of the relaxation function  $S(t)$  for propylene carbonate at 273 K in Fig. 6. At short times, the MSA and the present theory relax with almost the same slope, while the experimental results decay more slowly. At longer times, however, the MSA relaxes much more quickly than the theory presented here. At 298 K, a Cole–Davidson form was used for  $\epsilon(s)$ . Both the MSAS and the present theory predict relaxation rates of about 5 ps. This is slower than the experimentally observed relaxation of 2.4 ps. Figure 7 compares the experimental  $S(t)$  with theoretical predictions.

The other solvent treated in Table IV is propionitrile. In the propionitrile calculations, a Cole–Cole functional form was used for  $\epsilon(s)$ :

$$\epsilon(s) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + (s\tau_0)^{1-\alpha}} \quad (26)$$

For this particular solvent, the predictions of both theories are virtually identical and are in good agreement with experiment. The present theory of solvation offers a substantial improvement over dielectric continuum theory, as it reproduces the qualitative trends and departures from continuum behavior found in Table IV. Furthermore, improved approximations for  $c(k)$  can readily be built into the present theory. This cannot be done under the dynamical MSA.

## IV. CONCLUSION

In the present paper, we have derived a general theoretical framework for time-dependent solvation in polar solvents. This framework is based on using the experimental dielectric function  $\epsilon(s)$  to close the Mori hierarchy for polarization-density fluctuations. We have considered in detail the simplest application of this idea. This led to a theory where the static structure of the liquid enters through the direct correlation function  $c(k)$ . Dynamical aspects of solvation enter through the translation diffusion parameter  $p'$ , and  $\epsilon(s)$ . The present theory successfully predicts the qualitative trends in mean solvation time. Furthermore, the shape of the  $S(t)$  curve is often in good agreement with experiment. Non-Debye effects have been shown to be significant, particularly for the alcohols.

In our calculations, we have used the best currently available experimental results for  $\epsilon(s)$ . In many cases, however, the data on  $\epsilon(s)$  is not sufficiently accurate. Moreover, in our theory we mean  $\epsilon(s)$  to include frequencies up to and including the fastest solvation times.  $\epsilon_{\infty}$  characterizes electronic time scales, assumed to be much faster than solvation times. For experiments at cold temperatures, this corresponds to the microwave regime, where  $\epsilon(s)$  is traditionally measured. At room temperature however, the subpicosecond average solvation time commonly found clearly indicates that relevant time scales can be shorter than what can be probed in the microwave regime. The quantitative application of theories based on  $\epsilon(s)$  to solvents such as water will

TABLE IV. Relaxation times for nonhydrogenic polar solvents.

Solvent	$T(K)$	Form of $\epsilon(s)$	Data for $\epsilon(s)$	$d^*$	$p'$	$\tau_E^a/\tau^*$	$\tau_{MSA}^b/\tau^*$	$\tau^c/\tau^*$
Prop.carb.	298	Cole–Davidson	$\epsilon_0 = 66.4$ $\epsilon_{\infty} = 3.9$ $\tau_0 = 46.2$ ps $\beta = 0.91$	1.45	0.041	0.9	1.7	1.9
	252	Debye	$\epsilon_0 = 77.3$ $\epsilon_{\infty} = 10$ $\tau_D = 104$ ps			3.6	1.6	2.5
	237	Debye	$\epsilon_0 = 81.9$ $\epsilon_{\infty} = 10$ $\tau_D = 171$ ps			4.2	1.6	2.5
	221	Debye	$\epsilon_0 = 86.8$ $\epsilon_{\infty} = 10$ $\tau_D = 346$ ps			11	1.7	2.6
Propionitrile	298	Cole–Cole	$\epsilon_0 = 28.64$ $\epsilon_{\infty} = 2.0$ $\tau_0 = 4.7$ ps	1.44	0.042	2.6	1.9	1.8

<sup>a</sup> Experimental solvation time of Refs. 10 and 20 divided by  $\tau^*$ .

<sup>b</sup> Ionic solvation time predicted by the dynamical MSA, taken from Refs. 10 and 20.

<sup>c</sup> Ionic solvation time predicted by the present theory.

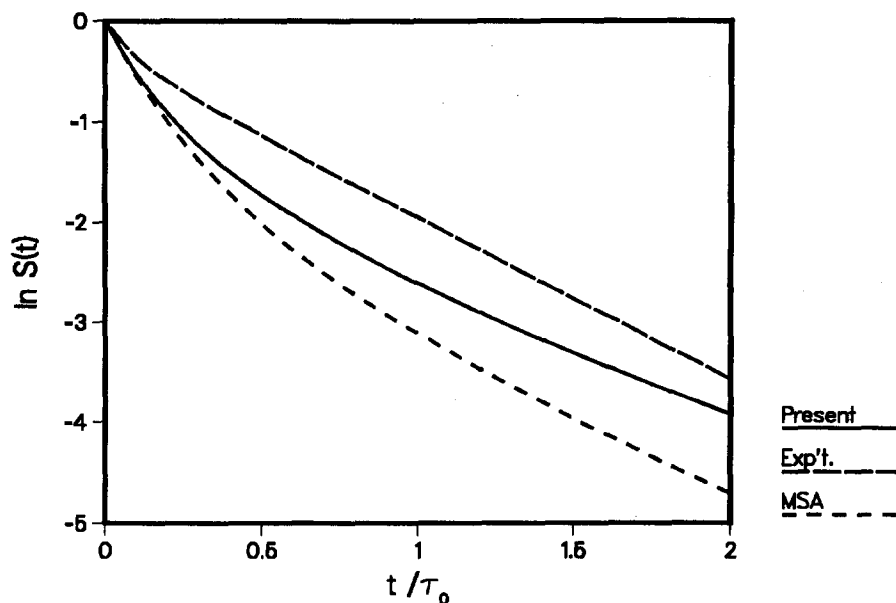


FIG. 6.  $\ln S(t)$  is shown for propylene carbonate at 273 K. Illustrated are experimental results (Ref. 20), results of the MSA (Ref. 20), and the results of the present theory.

require the incorporate of higher-frequency data into  $\epsilon$ , as well as generalizations of the theory to take into account molecular electronic polarizability.

For the sake of convenience, we have used the mean spherical approximation to provide the static direct correlation function. Nevertheless, the present theory does not depend on the MSA in any essential way. If better knowledge of the solvent's static structure is available, it can be incorporated. In particular, it is not necessary to assume a model of dipolar hard spheres for the solvent; the present theory leaves the door open for more realistic models or for the results of simulations. Also, it is not necessary to assume that the solute has a point charge distribution. Other distribution, including a point dipole and a finite dipole, can be treated by simply changing the applied field  $D(k)$ , and adding transverse relaxation if appropriate. These generalizations are clearly required for a quantitative theory of solvation. Thus, we view the present theory as a beginning rather than a

destination achieved. The wide range of possible extensions to the simple theory studied here is by far its greatest advantage.

*Note Added in Proof:* J. Barthel, K. Bachhuber, R. Buchner, and H. Hetzenauer [Chem. Phys. Lett. **165**, 369 (1990)] have recently reported new dielectric data for water and alcohols with enhanced high-frequency resolution. A. Kornyshev, A. Kuznetsov, D. Phelps, and M. Weaver [J. Chem. Phys. **91**, 7159 (1989)] have included molecular effects in solvation dynamics by postulating a functional form for  $\epsilon(k, \omega)$ . A similar functional form could be derived by expanding our formula for  $\alpha(k, s)$  to order  $k^2$ . This corresponds to a "near continuum" treatment of solvation.

#### ACKNOWLEDGMENTS

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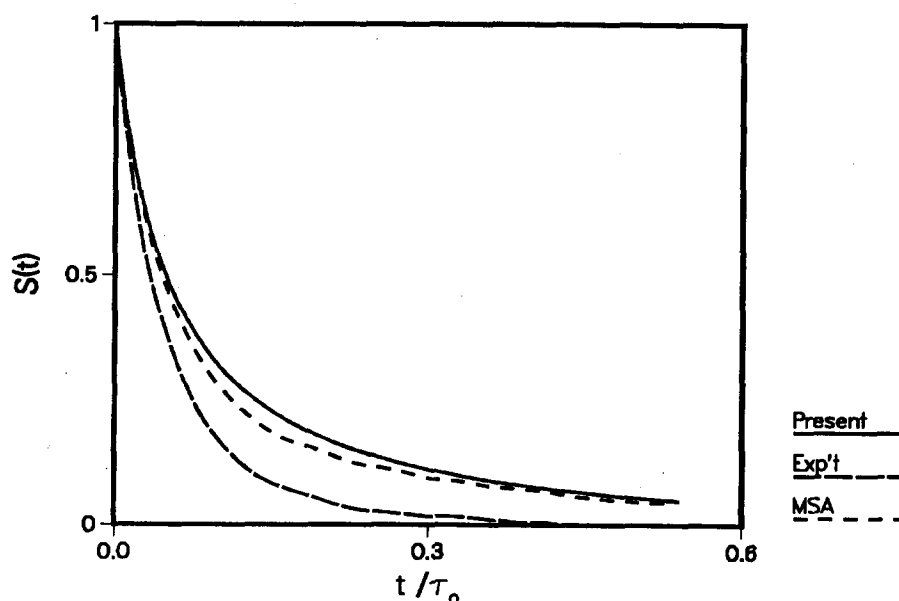


FIG. 7.  $\ln S(t)$  is given for propylene carbonate at 298 K. Experimental results (Ref. 10), results of the dynamical MSA (Ref. 10), and the results of the present theory are shown.

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## APPENDIX A

In this section, we give a detailed derivation of Eqs. (9) and (11) for the solvent polarizability. The physical interpretation of the approximations made here are discussed at length in Sec. II. First of all, we assume that the energy of solvation is given by the interaction energy of the pure solvent with a  $\mathbf{D}$  field cutoff at the solute radius. This approach has been used by Chandra and Bagchi in the study of time-resolved solvation.<sup>32-36</sup> Under this approximation, the solvent polarizability is diagonal in  $\mathbf{k}$ .

Using linear response theory,<sup>50</sup> we can relate the wave vector and frequency-dependent polarizability to the time-dependent dipole correlation function  $\langle \mu_{\mathbf{k}} \mu_{-\mathbf{k}} \rangle$ :

$$\alpha'(\mathbf{k}, s) = \beta V^{-1} \left\langle \mu_{\mathbf{k}} \mu_{-\mathbf{k}} - s \int_0^\infty dt e^{-st} \langle \mu_{\mathbf{k}}(t) \mu_{-\mathbf{k}}(0) \rangle \right\rangle, \quad (\text{A1})$$

where

$$\mu_{\mathbf{k}} = \sum_{i=1}^N \mu_i e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (\text{A2})$$

$\mu_i$  is the dipole moment of the  $i$ th solvent molecule, and  $\beta = 1/(k_B T)$ . The polarizability of the solvent to the vacuum electric field of the solute, and hence the energy of solvation, requires knowledge of the equilibrium correlation function  $\langle \mu_{\mathbf{k}}(t) \mu_{-\mathbf{k}} \rangle$ . In this correlation function the equilibrium distribution and the time evolution are governed by the Hamiltonian with the  $\mathbf{D}$  field switched off.

We now focus on the calculation of  $\langle \mu_{\mathbf{k}}(t) \mu_{-\mathbf{k}} \rangle$ . The vector  $\mu$  can be expressed as a moment of the position/orientation density  $\rho$  of the solvent:

$$\mu(\mathbf{r}) = |\mu| \int d\Omega \hat{\mathbf{n}}(\Omega) \rho(\mathbf{r}, \Omega), \quad (\text{A3})$$

where  $\hat{\mathbf{n}}(\Omega)$  is a unit vector in the direction given by  $\Omega$ . In the following discussion, we take the solvent molecules to be linear, and choose  $\Omega$  to describe the orientation of the molecular dipole moment. Also, we define the vector  $\mathbf{q}$  to be the set of all coordinates describing the solvent molecule:  $\mathbf{q} = (\mathbf{r}, \Omega)$ .

The generalized Langevin equation, developed by Mori<sup>51,52</sup> and Zwanzig,<sup>53</sup> gives a systematic framework for the evolution of time-dependent correlation functions. The generalized Langevin approach requires the identification of a set of functions of interest; we choose the continuous family of position/orientation density functions, given by

$$\delta\rho(\mathbf{q}) = \rho(\mathbf{q}) - \rho_0, \quad (\text{A4})$$

where  $\rho_0$  is the equilibrium density of particles.

We next consider the projection of an arbitrary function  $v$  onto the set  $\{\delta\rho(\mathbf{q})\}$ . We call this projection operator  $P$ , which is given by

$$Pv = \int d\mathbf{q} d\mathbf{q}' \langle \delta\rho(\mathbf{q}') v \rangle \Phi(\mathbf{q}', \mathbf{q}) \delta\rho(\mathbf{q}), \quad (\text{A5})$$

where  $\Phi$  satisfies

$$\int d\mathbf{q} \Phi(\mathbf{q}', \mathbf{q}) \langle \delta\rho(\mathbf{q}) \delta\rho(\mathbf{q}'') \rangle = \delta(\mathbf{q}' - \mathbf{q}''). \quad (\text{A6})$$

In other words,  $\Phi$  is the inverse of the overlap matrix  $\langle \delta\rho(\mathbf{q}) \delta\rho(\mathbf{q}'') \rangle$ .

The generalized Langevin equation for  $\langle \delta\rho(\mathbf{q}) \delta\rho(\mathbf{q}') \rangle$  is

$$\frac{d}{dt} \langle \delta\rho(\mathbf{q}; t) \delta\rho(\mathbf{q}') \rangle = - \int_0^t d\tau d\mathbf{q}'' K(\mathbf{q}, \mathbf{q}''; \tau) \times \langle \delta\rho(\mathbf{q}''; t - \tau) \delta\rho(\mathbf{q}') \rangle, \quad (\text{A7})$$

where  $Q = 1 - P$  is the complementary projection operator and

$$K(\mathbf{q}, \mathbf{q}'; t) = - \int d\mathbf{q}'' \{ [QL] \delta\rho(\mathbf{q}) \times e^{iQLt} [QL] \delta\rho(\mathbf{q}'') \} \Phi(\mathbf{q}'', \mathbf{q}'). \quad (\text{A8})$$

Equation (A7) is a formally exact equation of motion for the density. In the present article we evaluate the memory kernel using readily available information—the pair distribution function  $g(\mathbf{q}, \mathbf{q}')$  of the pure solvent (or equivalently the direct correlation function  $c$ ) and the dielectric function  $\epsilon(\omega)$ .

Certain “selection rules” apply to equilibrium expectation values. These rules are most transparently expressed if we transform to  $\mathbf{k}$  space. Next, we expand the angular dependence of  $\delta\rho(\mathbf{k}, \Omega)$  in terms of spherical harmonics. It is advantageous to use the  $\mathbf{k}$  frame<sup>30</sup> in this expansion, i.e., the wave vector  $\mathbf{k}$  is taken to lie along the  $z$  axis. Then we define

$$\delta\rho(\mathbf{k}, \Omega) = \sum_{l,m} \delta\rho(k, l, m) Y_{lm}(\Omega). \quad (\text{A9})$$

The translational invariance and isotropy of the medium implies that  $\langle \delta\rho(k_1, l_1, m_1; t) \delta\rho(k_2, l_2, m_2) \rangle$  is zero unless

$$k_1 = k_2, \quad m_1 = -m_2. \quad (\text{A10})$$

Different values of  $l$  are coupled. In the following discussion, correlation functions such as the direct correlation function  $c$  are expanded as

$$c(k, \Omega, \Omega') = \sum_{l_1, l_2, m} c(k, l_1, l_2, m) Y_{l_1, m}(\Omega) Y_{l_2, -m}(\Omega'). \quad (\text{A11})$$

In addition, we express the time dependence of all quantities in terms of the Laplace variable  $s$ , and we define the density fluctuation matrix  $\mathbf{d}$  as

$$\mathbf{d}(k, m; s)_{l_1, l_2} = \langle \delta\rho(k, l_1, m; s) \delta\rho(k, l_2, m) \rangle. \quad (\text{A12})$$

In this set of variables the equation of motion in Eq. (A7) becomes

$$\mathbf{d}(k, m; t = 0) - s\mathbf{d}(k, m; s) = \mathbf{K}(k, m; s) \cdot \mathbf{d}(k, m; s) \quad (\text{A13})$$

where

$$\mathbf{K}(k, m; s)_{l, l_2} = - \sum_l \left\langle [QL] \delta \rho(k, l, m) \frac{1}{s - iQL} \right. \\ \left. \times [QL] \delta \rho(k, l_3, -m) \right\rangle \Phi(k, l_3, l_2, m). \quad (\text{A14})$$

Equation (A13) has the solution

$$\mathbf{d}(k, m; s) = [\mathbf{K}(k, m; s) + s]^{-1} \cdot \mathbf{d}(k, m; t = 0), \quad (\text{A15})$$

where  $[\mathbf{K} + s]^{-1}$  denotes the matrix inverse with respect to  $l$ .

We propose to factorize the kernel  $\mathbf{K}$  as

$$\mathbf{K}(k, m; s) = \mathbf{K}(k, m, t = 0) r(s). \quad (\text{A16})$$

A similar factorization of the memory kernel has been used by Munakata<sup>54,55</sup> in the study of velocity self-diffusion in liquids. The Markovian approximation is a special case of the present factorization when  $r(s)$  is equal to a constant. Hence, we expect that factorization is, at the very least, accurate near the Markovian limit. Under the factorization approximation, the memory function at  $t = 0$  must be evaluated. We do this in Appendix B, and find that

$$K(k, l, l', m; t = 0) = -k_B T \{ l(l+1)/I + k^2/M \} \\ \times \{ (-1)^m - \rho_0 c(k, l, l', m) \}, \quad (\text{A17})$$

where  $c$  is the direct correlation function of the solvent,  $I$  is the solvent molecule's moment of inertia,  $M$  is its mass, and  $\rho_0$  is the equilibrium position/orientation density. The unknown relaxation function  $r(s)$  can be determined from the dielectric function  $\epsilon(s)$ . This can be done because  $\epsilon(s)$  is related to the  $l = 1$  and  $k = 0$  part of the density correlation function [Eq. (23)]. The present approximation is thus a partial resummation scheme which builds in experimentally determined non-Debye dielectric dispersion.

To see explicitly how the dielectric function can be used to close the Mori hierarchy, we first note that the longitudinal and transverse parts of the susceptibility are related to the corresponding wave vector and frequency dependent dielectric function:

$$\epsilon_L(k, s) = \{ 1 - 4\pi\alpha_L(k, s) \}^{-1}, \quad (\text{A18})$$

$$\epsilon_T(k, s) = 1 + 4\pi\alpha_T(k, s). \quad (\text{A19})$$

In the limit  $k \rightarrow 0$ , it is believed, on physical grounds<sup>23</sup> (though not mathematically proven), that

$$\epsilon_L(k = 0, s) = \epsilon_T(k = 0, s) \equiv \epsilon(s). \quad (\text{A20})$$

Let us consider  $\alpha_L$ . The usual dielectric function  $\epsilon(s)$  is equal to  $\epsilon(k = 0, s)$ . The longitudinal polarizability  $\alpha_L$ , however, is given by

$$\alpha'_L(k, s) = \beta V^{-1} \hat{\mathbf{k}} \cdot [ \langle \mu_{\mathbf{k}} \mu_{-\mathbf{k}} \rangle - s \langle \mu_{\mathbf{k}}(s) \mu_{-\mathbf{k}} \rangle ] \cdot \hat{\mathbf{k}}. \quad (\text{A21})$$

$\alpha'_L(s)$  can be expressed in terms of the density fluctuation matrix as

$$\alpha'_L(k, s) = \frac{4\pi\beta |\mu|^2}{3} [ \mathbf{d}(k, 0; t = 0)_{1,1} - s \mathbf{d}(k, 0; s)_{1,1} ]. \quad (\text{A22})$$

Plugging this result into Eq. (A15) then gives

$$\alpha'_L(k, s) = \frac{4\pi\beta}{3} |\mu|^2 \sum_l \left[ \delta_{l,1} - \frac{s}{\mathbf{K}(t=0)r(s) + s} \right]_{1,l'} \\ \times [ \rho_0^2 h(k, l', 1, 0) + \rho_0 ]. \quad (\text{A23})$$

Since  $\alpha(k = 0, s)$  is known through Eq. (A18), we can solve Eq. (A23) for  $r(s)$ .

A particularly simple result is obtained if we assume that the memory kernel  $\mathbf{K}$  does not couple different  $l$  values. This is the angular decoupling approximation discussed in Sec. II. The decoupling approximation holds within the MSA. The following intermediate result is then derived by considering the  $k = 0$  and  $s = 0$  polarizability, along with Eq. (A18):

$$\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} = \frac{(4\pi)^2 \beta |\mu|^2 \rho_0}{3 [ 1 - \rho_0 c_L(0) ]}. \quad (\text{A24})$$

This constitutes a relationship between the parameters of the polar model [right-hand side of Eq. (A24)], and the measured dielectric function of the solvent [left-hand side of Eq. (A24)]. This leads directly to Eq. (9). The same approach used for the longitudinal polarizability can be used for the transverse polarizability.

## APPENDIX B

In this Appendix we evaluate the  $t = 0$  memory function  $K(\mathbf{q}, \mathbf{q}', t = 0)$ . To keep these results as general as possible, we do not assume a uniform solvent. According to the definition of the memory function, Eq. (A8), the  $t = 0$  memory function is equal to

$$K(\mathbf{q}, \mathbf{q}'; t = 0) = \int d\mathbf{q}'' \langle [iQL\delta\rho(\mathbf{q})] \\ \times [iQL\delta\rho(\mathbf{q}'')] \rangle \Phi(\mathbf{q}'', \mathbf{q}'). \quad (\text{B1})$$

But since  $iL\delta\rho(\mathbf{q}) = d\delta\rho(\mathbf{q})/dt \equiv \dot{\delta\rho}(\mathbf{q})$ , and  $P\dot{\delta\rho}(\mathbf{q}) = 0$ , we have

$$K(\mathbf{q}, \mathbf{q}'; t = 0) = \int d\mathbf{q}'' \langle \dot{\delta\rho}(\mathbf{q}) \dot{\delta\rho}(\mathbf{q}'') \rangle \Phi(\mathbf{q}'', \mathbf{q}'). \quad (\text{B2})$$

Thus, we need to explicitly evaluate both  $\Phi$  and  $\langle \dot{\delta\rho}(\mathbf{q}) \dot{\delta\rho}(\mathbf{q}') \rangle$ . We turn first to the evaluation of  $\Phi$ . To do so, we introduce the radial distribution function of the non-uniform fluid

$$g^{(2)}(\mathbf{q}, \mathbf{q}') = \frac{\langle \sum_{i \neq j} \{ \delta(\mathbf{q} - \mathbf{q}_i) \delta(\mathbf{q}' - \mathbf{q}_j) \} \rangle}{[\rho_0(\mathbf{q}) \rho_0(\mathbf{q}')]}. \quad (\text{B3})$$

The correlation function  $\langle \rho(\mathbf{q}) \rho(\mathbf{q}') \rangle$  can be expressed in terms of  $g^{(2)}$ ,

$$\langle \rho(\mathbf{q}) \rho(\mathbf{q}') \rangle = \rho_0(\mathbf{q}) \rho_0(\mathbf{q}') g^{(2)}(\mathbf{q}, \mathbf{q}') \\ + \rho_0(\mathbf{q}') \delta(\mathbf{q} - \mathbf{q}'). \quad (\text{B4})$$

Finally, we need the generalization of the Ornstein-Zernicke equation to nonuniform fluids

$$h(\mathbf{q}, \mathbf{q}') = c(\mathbf{q}, \mathbf{q}') + \int d\mathbf{q}'' c(\mathbf{q}, \mathbf{q}'') h(\mathbf{q}'', \mathbf{q}') \rho_0(\mathbf{q}''), \quad (\text{B5})$$

where  $h = g^{(2)} - 1$ . With these ingredients, one can readily verify that

$$\Phi(\mathbf{q}, \mathbf{q}') = \frac{\delta(\mathbf{q} - \mathbf{q}')}{\rho_0(\mathbf{q})} - c(\mathbf{q}, \mathbf{q}'). \quad (\text{B6})$$

Next, we evaluate the expectation value  $\langle \delta\rho(\mathbf{r}, \Omega) \delta\rho(\mathbf{r}', \Omega') \rangle$ . To begin with, we show that the two-body terms vanish. It suffices to show that

$$\left\langle \frac{d}{dt} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\Omega - \Omega_i) \frac{d}{dt} \delta(\mathbf{r}' - \mathbf{r}_j) \delta(\Omega' - \Omega_j) \right\rangle = 0. \quad (\text{B7})$$

This term is of the form  $\langle \dot{f}(\mathbf{q}_i) \dot{f}(\mathbf{q}_j) \rangle$ , where  $\mathbf{q}_i$  denotes a vector containing all canonical coordinates associated with particle  $i$ . This expectation value is equal to

$$Z^{-1} \int d\mathbf{q}_1 \cdots d\mathbf{q}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N \left[ \frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial f}{\partial \mathbf{q}_i} \right] \left[ \frac{\partial H}{\partial \mathbf{p}_j} \cdot \frac{\partial f}{\partial \mathbf{q}_j} \right] e^{-\beta H}, \quad (\text{B8})$$

which can be rearranged to give

$$Z^{-1} \int d\mathbf{q}_1 \cdots d\mathbf{q}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N \left[ \frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial f}{\partial \mathbf{q}_i} \right] \times \left[ \frac{\partial f}{\partial \mathbf{q}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j} \{ -e^{-\beta H} / \beta \} \right]. \quad (\text{B9})$$

Integrating by parts with respect to  $\mathbf{p}_j$  then yields

$$(Z\beta)^{-1} \int d\mathbf{q}_1 \cdots d\mathbf{q}_N d\mathbf{q}_1 \cdots d\mathbf{p}_N \frac{\partial f}{\partial \mathbf{q}_j} \times \frac{\partial^2 H}{\partial \mathbf{p}_i \partial \mathbf{p}_j} \cdot \frac{\partial f}{\partial \mathbf{q}_i} e^{-\beta H}. \quad (\text{B10})$$

But,  $\partial^2 H / \partial \mathbf{p}_i \partial \mathbf{p}_j = 0$ , since the derivatives refer to different particles. As a direct result, there are only one-body terms in  $\langle \delta\rho(\mathbf{r}, \Omega) \delta\rho(\mathbf{r}', \Omega') \rangle$ .

We now evaluate these one-body terms. Let  $(\mathbf{q}, \mathbf{p})$  denote the canonical coordinates and momenta of the particle of interest, and let  $q^{(i)}$  denote the  $i$ th canonical coordinate of that particle, and  $p^{(j)}$  denote the  $j$ th canonical momenta of that particle. Then

$$\langle \delta(\mathbf{q}' - \mathbf{q}) \delta(\mathbf{q}'' - \mathbf{q}) \rangle = \sum_{ij} \left\langle \left[ \frac{\partial \delta(\mathbf{q}' - \mathbf{q})}{\partial q^{(i)}} \dot{q}^{(i)} \right] \times \left[ \frac{\partial \delta(\mathbf{q}'' - \mathbf{q})}{\partial q^{(j)}} \dot{q}^{(j)} \right] \right\rangle. \quad (\text{B11})$$

By the same arguments given above, it can be shown that terms with  $i \neq j$  vanish, unless  $\partial^2 H / \partial \mathbf{p}^{(i)} \partial \mathbf{p}^{(j)} \neq 0$ . Since there are no such terms in  $H$ , only terms with  $i = j$  persist. The evaluation of these terms is quite straightforward. We find a translational contribution of

$$-\frac{kT}{m} \nabla \cdot \rho_0(\mathbf{r}', \Omega') \nabla \delta(\mathbf{r}' - \mathbf{r}'') \delta(\Omega' - \Omega''), \quad (\text{B12})$$

and a rotational contribution of

$$-\frac{kT}{I} \mathbf{L} \cdot \rho_0(\mathbf{r}', \Omega') \mathbf{L} \delta(\mathbf{r}' - \mathbf{r}'') \delta(\Omega' - \Omega''). \quad (\text{B13})$$

Equations (B6), (B12), and (B13) give the following result for the  $t = 0$  memory kernel:

$$K(\mathbf{q}, \mathbf{q}'; t = 0) = - \{ (kT/I) \mathbf{L} \cdot \rho_0(\mathbf{q}) \mathbf{L} + (kT/m) \nabla \cdot \rho_0(\mathbf{q}) \nabla \} \times \left\{ \frac{\delta(\mathbf{q} - \mathbf{q}')}{\rho_0(\mathbf{q})} - c(\mathbf{q}, \mathbf{q}') \right\}. \quad (\text{B14})$$

For the special case of an isotropic medium this reduces to

$$K(\mathbf{q}, \mathbf{q}'; t = 0) = -\rho_0 \{ (k_B T / I) \mathbf{L}^2 + (k_B T / M) \nabla^2 \} \times \left\{ \frac{\delta(\mathbf{q} - \mathbf{q}')}{\rho_0} - c(\mathbf{q}, \mathbf{q}') \right\}. \quad (\text{B15})$$

When expressed in the  $k$  frame, this result is equivalent to Eq. (A17).

## APPENDIX C

Above, we presented a theory of solvation in polar fluids that was based on using a factorization approximation for the memory function  $\mathbf{K}$ . In this Appendix, we outline how such an approximation can be systematically improved. A principal improvement of the above theory would be to take better account of cooperative solvent motions. In the framework considered here, this would mean using a more sophisticated approximation for the memory kernel. In the following discussion, we no longer show explicitly the  $k$  and  $m$  dependence of  $\mathbf{K}$ . The comments made below can apply to a nonisotropic medium (i.e., the cutoff function approximation for  $\alpha$  can be relaxed). In this case, however,  $k$  and  $m$  are no longer constants of the motion, and should be regarded as matrix indices.

The continued fraction expansion of the memory kernel  $\mathbf{K}^{s2}$  can be introduced by invoking an infinite hierarchy of memory functions. In this notation, the hierarchy of memory functions is given by

$$[s + \mathbf{K}^{(n)}(s)] \mathbf{K}^{(n-1)}(s) = \mathbf{K}^{(n-1)}(t = 0). \quad (\text{C1})$$

A continued fraction expansion for  $\mathbf{K}^{(1)}$  can be derived by repeatedly applying Eq. (C1). This gives us

$$\mathbf{K}(s) = \frac{1}{s + (1/[s + \cdots \Delta_3]) \Delta_2} \Delta_1, \quad (\text{C2})$$

where  $\Delta_n = \mathbf{K}^{(n)}(t = 0)$ . The continued fraction, if truncated at  $n$ th order, requires knowledge of the memory function  $\mathbf{K}^{(n)}(s)$ . Thus, an approximation must be used for  $\mathbf{K}^{(n)}$ . It is conventional to use the Markovian approximation on the  $n$ th level:  $\mathbf{K}^{(n)}(s) = \gamma \mathbf{K}^{(n)}(t = 0)$ . It is possible, however, to make the factorization approximation on the  $n$ th level as well:

$$\mathbf{K}^{(n)}(s) = \mathbf{K}^{(n)}(t = 0) r(s). \quad (\text{C3})$$

As was done in Appendix A, the experimentally known dielectric function  $\epsilon(s)$  can be used to solve for  $r(s)$ . For a nonisotropic medium, however, the dielectric function in the presence of the solute must be used. This is not usually available from experiment, but could be calculated from simulations.

Next, we give explicit formulas for the hierarchy of memory functions used in Eq. (C1). These results are the generalization to a multidimensional  $P$  space of the continued fraction expansion of the memory kernel employed by Mori<sup>52,51</sup> and reviewed by Berne and Harp.<sup>50</sup> We consider a  $P$  space spanned by a set of classical functions  $f^{(0)}(\mathbf{q})$ , where  $\mathbf{q}$  is an index (possibly continuous) labeling the functions. The functions are assumed to have the same time reversal symmetry. In the present case,  $f^{(0)}(\mathbf{q}) = \delta\rho(\mathbf{q})$ , where  $\mathbf{q} = (\mathbf{r}, \Omega)$ . It is most convenient to use a notation that brings

forth the Hilbert space structure of classical mechanics. To do so, we call the classical function  $A(\mathbf{q})$  a ket:

$$|A(\mathbf{q})\rangle \equiv A(\mathbf{q}), \quad (\text{C4})$$

and define the inner product

$$\langle A(\mathbf{q})|B(\mathbf{q}')\rangle = \langle A(\mathbf{q})B(\mathbf{q}')\rangle, \quad (\text{C5})$$

where  $\langle \rangle$  is the classical expectation value. Then the following recursion relations:

$$L_n = Q_{n-1} L_{n-1} Q_{n-1}, \quad (\text{C6})$$

$$|f^{(n)}\rangle = iQ_{n-1} L_{n-1} |f^{(n-1)}\rangle, \quad (\text{C7})$$

$$\mathbf{S}^{(n)}(\mathbf{q}, \mathbf{q}') = \langle f^{(n)}(\mathbf{q})|f^{(n)}(\mathbf{q}')\rangle, \quad (\text{C8})$$

$$\Phi^{(n)}(\mathbf{q}, \mathbf{q}') = [\mathbf{S}^{(n)}]^{-1}(\mathbf{q}, \mathbf{q}'), \quad (\text{C9})$$

$$Q_n(\mathbf{q}, \mathbf{q}') = \delta(\mathbf{q} - \mathbf{q}') - |f^{(n)}(\mathbf{q})\rangle \times \Phi^{(n)}(\mathbf{q}, \mathbf{q}') \langle f^{(n)}(\mathbf{q}')|, \quad (\text{C10})$$

and the initial conditions

$$L_0 = L, \quad (\text{C11})$$

$$Q_0 = Q \quad (\text{C12})$$

lead to the following equation for the  $n$ th memory function:

$$K^n(\mathbf{q}, \mathbf{q}'; s) = - \langle Q_{n-1} L_{n-1} f^{(n-1)}(\mathbf{q}) | \frac{1}{s - iL_n} \times |Q_{n-1} L_{n-1} f^{(n-1)}(\mathbf{q}'')\rangle \times \Phi^{(n-1)}(\mathbf{q}'', \mathbf{q}') \rangle. \quad (\text{C13})$$

## APPENDIX D

In this Appendix, we give explicit equations for  $c_L(k)$  within the MSA. These results are well known,<sup>30</sup> and are given here to keep the presentation self-contained. In the following discussion, it is convenient to use units where the solvent diameter is equal to 1. The longitudinal part of the direct correlation function  $c$  is

$$c_L(k) = 8\pi K c_{PY}(k, 2K\eta), \quad (\text{D1})$$

where  $c_{PY}(k, \eta)$  is the Percus–Yevick result for a nondipolar hard sphere fluid at packing ratio  $\eta \equiv \pi\rho/6$ . This is given by

$$c_{PY}(r) = \begin{cases} -\lambda_1 - 6\eta\lambda_2 r - \eta\lambda_1 r^3/2, & r < 1 \\ 0, & r > 1 \end{cases}, \quad (\text{D2})$$

where

$$\lambda_1 = (1 + 2\eta)^2 / (1 - \eta)^4, \quad (\text{D3})$$

$$\lambda_2 = -(1 + \frac{1}{2}\eta)^2 / (1 - \eta)^4. \quad (\text{D4})$$

The parameter  $K$  can be expressed in terms of  $\epsilon_0$

$$\epsilon_0 = Q(2K\eta) / Q(-K\eta), \quad (\text{D5})$$

where

$$Q(\eta) = (1 + 2\eta)^2 / (1 - \eta)^4. \quad (\text{D6})$$

To show that Eq. (9) does not depend explicitly on  $\rho$  within the MSA, we note that  $c_L$  is always multiplied by  $\rho$ . Equation (D1) gives

$$\rho c_L(k) = 48K\eta c_{PY}(k, 2K\eta). \quad (\text{D7})$$

Equation (D5), however, implies that  $K\eta$  is a function of  $\epsilon_0$ . Thus,  $\rho c_L(k)$  is a function of  $\epsilon_0$  only, and does not depend explicitly on  $\rho$ .

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