The dynamics of polar solvation: Inhomogeneous dielectric continuum models

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The influence of an inhomogeneous dielectric response on the dynamics of solvation of ions and dipoles is investigated. Solvent models considered include discrete shell models as well as models in which the solvent dielectric constant varies continuously as a function of distance from a spherical solute. The effect of such dielectric inhomogeneity is to introduce additional, slower relaxation times into the solvation response when compared to the homogeneous case. For all models studied, the deviation of the average relaxation time from that predicted for a homogeneous continuum solvent increases as the dielectric constant and the length parameter, which specifies the rapidity of approach to bulk behavior, increase. For a given solvent model the solvation response to a change in a point dipole moment is slower than the response to a charge jump. The continuum results are compared to a recent molecular model based on the mean spherical approximation. The comparison suggests that deviations from homogeneous continuum behavior in the molecular model can be accounted for by inhomogeneity of the solvent dielectric constant extending only over the first solvation shell. Predictions of inhomogeneous continuum models are also compared to experimental data. Both the observed dependence of average relaxation time on dielectric constant, and the detailed time dependence of the relaxation in high dielectric constant solvents can be rationalized on the basis of such models.

I. INTRODUCTION

The energetics of solvation is of central importance in determining reaction dynamics in polar solvents. In addition to the long appreciated influences that equilibrium solvent properties have on reaction rates, a growing body of literature points to the important role that dynamical solvent effects play in many types of reactions. For this reason, the nonequilibrium dynamics of solvation of a newly created charge or dipole moment has begun to receive considerable attention from both experimental and theoretical perspectives. Advances in subpicosecond laser spectroscopy have made possible the study of the dynamics of polar solvation directly in the time domain. Although the details are far from clear, certain general trends now seem evident in the experimental data collected by several groups. A number of theoretical approaches have also been employed in modeling the dynamics of polar solvation. These studies have provided a good deal of insight into the problem; however, a quantitative understanding of the emerging experimental results is still lacking.

The objective of the present paper is to describe a new theoretical calculation of the dynamics of solvation in a polar liquid. The approach we take is based on a continuum model for solvent. It differs from earlier continuum calculations that treated the solvent as a uniform dielectric fluid in that we now consider the effect of inhomogeneity of the solvent dielectric response in the vicinity of the solute molecule. That is, we postulate that the dielectric constant varies in some manner as a function of distance from the solute and explore the dynamical consequences for both ionic and dipolar solutes. (The physical basis for such dielectric inhomogeneity will be discussed shortly.) We show that fairly simple solutions for the dynamics can be obtained in many cases. These solutions exhibit semiquantitative agreement with experimentally observed trends for reasonable choices of the solvent model parameters. In addition to comparing our calculations to experimental results, we also make the comparison to a recent molecular model of solvation dynamics. The similarities observed between the results of these contrasting models provide further insight into the physical content of both models, and into the dynamics of polar solvation.

The first theoretical models to treat the dynamics of solvation in polar liquids began with a picture of the solvent as a homogeneous continuum characterized by its bulk dielectric dispersion, $\epsilon(\omega)$. The solute was viewed as a spherical cavity having dielectric constant $\epsilon_c$ and containing a centered point charge or dipole. A value of $\epsilon_c$ different from unity was used to represent the solute polarizability. These pictures represent dynamic extensions of the venerable models used by Born, Onsager, and many others to investigate equilibrium aspects of solvation. Dynamical predictions of such homogeneous continuum theories are most simply discussed in terms of a normalized response function
\[ S(t) = \frac{E(t) - E(\infty)}{E(0) - E(\infty)}, \quad (1.1) \]

where \( E(t) \) is the free energy of solvation at a time \( t \) after an instantaneous change in the solute charge or dipole moment. In the case of a single Debye type \( \epsilon(\omega) \),

\[ \epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega \tau_D}, \quad (1.2) \]

homogeneous continuum models predict that the energy relaxation is exponential,

\[ S_\alpha(t) = \exp(-t/\tau_\alpha), \quad (1.3) \]

with time constant \( \tau_\alpha \) given by

\[ \tau_\alpha = \left( \frac{\epsilon_\infty + \alpha_n \epsilon_c}{\epsilon_0 + \alpha_n \epsilon_c} \right) \tau_D, \quad (1.4) \]

with \( \alpha_n = n/(n + 1) \). In these expressions \( n \) designates the response due to a jump in the solute’s \( n \)th order multipole moment. Thus, \( n = 0 \) denotes a charge jump and the solvation time is predicted to be the solvent longitudinal relaxation time, \( \tau_L = \tau_0 = (\epsilon_\infty/\epsilon_0) \tau_D \). For a dipole change \( (n = 1) \) the response time is slightly longer,

\[ \tau_1 = \left( \frac{2\epsilon_\infty + \epsilon_c}{2\epsilon_0 + \epsilon_c} \right) \tau_D, \quad (1.5) \]

However, under the usual assumption that \( \epsilon_c = 1 \) and for typical values of \( \epsilon_\infty \) and \( \epsilon_0 \), \( \tau_1 \) differs from \( \tau_L \) only about 10%. Given the simplicity of the model, such a distinction between different multipole moments is unimportant and we may simply state that the prediction of homogeneous continuum models is that the solvent free energy should relax exponentially with time constant given by the solvent longitudinal relaxation time. This \( \tau_L \) time constant is much shorter than the Debye time, \( \tau_D \), or the comparable single-particle reorientation time of the solvent, as a result of cooperative motions of large numbers of molecules. In some sense the ratio \( \epsilon_c/\epsilon_0 \), by which \( \tau_L \) differs from \( \tau_D \), is a gauge of the degree of cooperativity of the solvation response. It should be pointed out that this simple exponential relaxation is predicted by homogeneous continuum models only for the case of a Debye dielectric response \([\text{Eq. (1.2)}]\). For more complicated \( \epsilon(\omega) \) the response is nonexponential and has been examined in detail Ref. 20.

Experimental measurements of solvation time scales usually entail measuring the time dependent fluorescence Stokes shift after ultrafast excitation. A wide variety of dipolar solute/polar solvent systems have been considered in recent studies. The uncharged, rigid molecules 1-aminonaphthale,4 4-aminophthalamide,8,13 Coumarins 153,10,14 102,14 and 31114 have been used as fluorescence probes. Molecules with more complicated photophysics, e.g., LDS-750,9 bianthralk,14 4-(9-anthryl)-N,N-dimethylaniline,13 bis (4-dimethylaminophenyl) sulfone,15 and Nile Red12 have also been studied. The dynamics in solvents ranging from highly associated hydrogen bonding solvents such as \( n \)-alcohols and amides,6-13,15 as well as aprotic solvents such as \( n \)-nitriles,14 glycerol triacetate,13 DMSO,9 and propylene carbonate10,14 have been measured in this way. Experimental results are usually analyzed in terms of a spectral shift re-

response function \( C(t) \) defined as

\[ C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}, \quad (1.6) \]

where the \( \nu 's \) are frequencies of some characteristic feature of the emission spectrum at times \( t, \) zero, and infinity. Under the assumption of a linear solvent response (an assumption made in all existing theories) this experimental spectral shift function is directly comparable to the energy relaxation response function \( S(t) \) calculated theoretically.

The major results of the above experiments may be summarized as follows. (i) The observed solvation times are largely probe independent and appear to reflect mainly properties of the solvents studied. Thus while some discrepancies among the behavior of different probes molecules exist, the solvation times measured for a given solvent with different probes usually agree to within a factor of 2.11,14 (ii) Solvation times are generally longer than the \( \tau_L \) prediction and usually lie between \( \tau_0 \) and \( \tau_\alpha \). In some instances, solvation times were measured to be more than an order of magnitude longer than \( \tau_L \).10 (iii) There appears to be a correlation between the deviation from \( \tau_L \) and the static dielectric constant \( \epsilon_0 \) (or \( \epsilon_0/\epsilon_\infty \), see Fig. 16).10 (iv) In cases where the Stokes shift could be followed for many lifetimes, the observed \( C(t) \) functions were clearly nonexponential in contrast to simple continuum predictions.10 These \( C(t) \) curves could often be well represented by a stretched exponential form, \( \exp \left[-(t/T_L)\alpha\right] \) with exponent \( \alpha \) significantly less than unity.10 Such behavior is well known for relaxation in glass-like systems10 and implies the presence of a continuous distribution of relaxation times in the solvation process rather than a single time as predicted by homogeneous continuum models. The above results clearly point out that simple continuum treatments are inadequate for understanding solvation in real liquids. An obvious conclusion is that molecular aspects of solvation, totally neglected by these initial models, are in fact important in determining the observed dynamics. Models which either begin from a purely molecular viewpoint, or that at least incorporate some molecular features, seem necessary to achieve a better understanding.

One way to gain more insight into molecular aspects of the solvation process is through the use of molecular dynamics (MD) computer simulations. In this case one “experiments” with a molecular model which is exactly solvable numerically. Maroncelli and Fleming11 have performed such MD simulations of solvation of spherical ions in ST2 water. A related study of spherical dipolar solutes was carried out by Karim et al.32 using the TIPS4P model of water. The dynamics observed in both studies depended in a complicated way on the size and charge of the solute as well on whether a jump in the solute’s charge, dipole, or quadrupole moment was considered. Response times both faster and slower than \( \tau_L \) were observed, unlike the experimental situation where observed response times are almost always slower than \( \tau_L \). It appears that the highly structured surroundings of a solute in aqueous solution makes the dynamics much more solute specific than in other, simpler solvents. Although water may not be representative of most solvents, the simulations do provide clues as to why the experimentally
observed dynamics deviate from predictions of simple continuum theories. As with the experiments, the response functions observed in these water simulations were nonexponential. One source of this nonexponentiality was found to be that regions of the solvent at different distances from the solute react at different rates. Such behavior was first predicted by Onsager who suggested that in the solvation of a newly formed electron the far away solvent should equilibrate first and the nearest neighbor solvent molecules last. While the ordering of response times is not always observed to be in the direction predicted by Onsager, the idea of the nonequivalence of different solvent regions is an important motivation for our use of inhomogeneous continuum models.

Several theoretical investigations of solvation dynamics have employed molecular models for the solvent in an attempt to better understand the experimental and simulated results. Actually, even before most of these recent results became available, Calef and Wolynes carried out a detailed study of the problem of ionic solvation. The authors utilized a Smoluchowski-Vlasov equation to study relaxation of the polarization field around a newly created charge. They found that the polarization closest to the charge is slower than that at large distances, which is in agreement with Onsager's prediction and simulation results. These authors also found that the relaxation of the electrostatic energy is nonexponential, and the average relaxation time is closer to \( \tau_L \) than to \( \tau_D \). This is again in keeping with the experimental findings. In a different study, Loring and Mukamel developed a general formalism to treat the dielectric response of a polar liquid to a newly created ion paying proper attention to relaxation occurring on molecular length scales. These authors studied the polarization response of a lattice of point dipoles undergoing Brownian reorientational motion when a charge is instantaneously placed on a lattice site. Relaxation of the polarization of the surrounding lattice was found to show a behavior similar to that predicted by Calef and Wolynes. Loring and Mukamel pointed out that in the presence of dipole–dipole interactions it is not possible to define a single relaxation time, like \( \tau_L \), to characterize the solvent response. A similar conclusion was reached by Friedrich and Kivelson who also examined the linear response of a fluid to the sudden imposition of an ionic charge. These authors concluded that response of the solvent depends on all length scales. Only the relaxation at longer length scales can be described by a continuum model, while the relaxation occurring on molecular length scales is characterized by single particle motions. Thus, the response will consist of a infinite number of relaxation times ranging between \( \tau_L \) (the continuum limit) and a single particle time scale closer to \( \tau_D \). All three of the above theories have provided insight into how molecular effects cause dynamics in real liquids to deviate from continuum predictions. Unfortunately none of them were able to provide direct quantitative comparison to experimental data.

Very recently, one such molecular model has been developed based on the well-known mean spherical approximation (MSA) treatment of polar liquids. Wolynes has generalized the work of Chan et al. to model the dynamics of ionic solvation of a hard-sphere ion in a hard-sphere dipolar liquid. In his initial study, Wolynes obtained only approximate solutions for the dynamics within this MSA model. In later work, Rips, Klafter, and Jortner and Nichols and Calef were able to obtain exact solutions for the dynamical MSA model. In agreement with the studies mentioned above, this molecular model also predicts nonexponential relaxation of the solvation energy that should occur over a range of time scales between \( \tau_L \) and \( \tau_D \). The great virtue of the dynamical MSA model is that it is simple enough to allow straightforward comparison to experimental results. The solvent’s dynamics are obtained empirically from the bulk \( \epsilon(\omega) \) dispersion. Molecular aspects of the solvation structure affect the dynamics via the structure-dependent relationship between \( \epsilon \) and the solvation energy. The structure surrounding an experimental solute/solvent combination is assumed to be adequately described by the analogous structure of a reference hard-sphere ion/dipolar hard-sphere system, obtained from an MSA treatment. Predictions of this dynamical MSA model thus depend only on \( \epsilon(\omega) \) of the solvent and on the relative sizes of the solute and solvent molecules. Maroncelli and Fleming have recently made a detailed comparison of experimental fluorescence results to predictions of this model. They found that the dynamical MSA model was able to provide a semiquantitative account of the main trends in the experimental data.

In the present paper we take a different approach to understanding why experimentally observed dynamics deviate from predictions based on simple continuum models. Rather than beginning with a molecular (but necessarily crude) solvent model, as was done in the above studies, we instead work with a continuum solvent and consider how inhomogeneity of the dielectric constant affects the dynamics. That is, we acknowledge the finite size of solvent molecules by introducing a distance dependent dielectric function \( \epsilon(r) \) that allows the bulk dielectric constant \( \epsilon_B \) to be achieved gradually over the first few solvent shells as the distance from the solute increases. It has long been appreciated that the original Born/Onsager treatments, in which \( \epsilon_B \) pertains immediately outside of the solute cavity, over estimate solvation energies for unbiased choice of solute size. Many workers have considered the use of such phenomenological \( \epsilon(r) \) functions to remedy this problem. For example, Abraham and Lisz showed that a single solvent-sized shell about the solute with reduced dielectric constant (\( \epsilon = 2 \)) was able to account for observed solvation free energies of monovalent ions much better than could the original continuum models. More complicated multiple shell schemes as well as continuous \( \epsilon(r) \) functions have been proposed to further enhance agreement with observed solvation energies. All of these inhomogeneous continuum models attempt to account for some aspects of solvent molecularity while preserving the relative simplicity of the solutions afforded by continuum electrostatics.

Several aspects of molecular solvation can be mimicked using an effective dielectric constant that decreases from the bulk value as one approaches within a few solvent diameters of a solute. The first is due to the nonlocality of the solvent dielectric response. The polarization response of a
solvent to a spatially varying electric field depends on how rapidly in terms of a wave-vector dependent dielectric function $\epsilon(k)$. Macroscopic fields usually vary slowly over molecular length scales and one normally only need consider the static dielectric constant $\epsilon_0 = \epsilon(k=0)$. The field created by a molecular ion or dipole, however, changes dramatically over dimensions comparable to the solvent size. Thus large $k$ components of $\epsilon(k)$ [where $\epsilon(k) \to 1$] contribute substantially to the solvation response and decrease the solvation energy compared to what is expected from $\epsilon_0$ alone. While the high $k$ behavior of $\epsilon(k)$ has not been measured experimentally, Kornyshev\textsuperscript{44} has shown that for certain simple functional forms of $\epsilon(k)$ the nonlocality can be treated in terms of a spatially dependent dielectric constant $\epsilon(r)$. The deviation from a simple continuum picture due to nonlocality is a manifestation of the molecular nature of the solvent in the absence of solute. The solute can also modify the characteristics of the solvent in its own neighborhood. For example, it is well known that the structure of water near to a solute differs from that of bulk water in a way that depends on the solute’s hydrophobic or hydrophilic character.\textsuperscript{45} Such differences can be modeled in terms of a slightly different dielectric constant near to the solute. More commonly, $\epsilon(r)$ functions have been invoked to account for “dielectric saturation” near to an ion or large dipolar solute.\textsuperscript{38,39} Electric fields in the neighborhood of small ionic or dipolar solutes are quite large and often exceed the field strengths for which linear dielectric response is expected.\textsuperscript{46–48} The normal situation at high field strengths is that the polarization is less than that which would hold in a linear regime,\textsuperscript{49} i.e., the polarization begins to saturate. This effect can also be modeled in terms of an effective $\epsilon(r)$ that decreases from the bulk to a spatially varying value.

Although the above molecular mechanisms motivate the use of inhomogeneous continuum models, there is no precise connection between the solvation structure in a molecular liquid and a continuum $\epsilon(r)$ function.\textsuperscript{44} Our purpose in the present work is therefore not to propound any new models. We first treat the discrete shell model and then explore the dynamical consequences of several simple functional forms of $\epsilon(r)$. In the Appendix we examine the dynamics of solvation of an ion in an inhomogeneous solvent consisting of either multiple homogeneous shell regions or a continuous $\epsilon(r)$ function. In the ionic solvation case the results derived are quite simple and intuitive. The case of a dipolar solute, although physically similar, is mathematically more complicated and is treated in the Appendix. In Sec. III we describe the dynamical behavior predicted from a number of $\epsilon(r)$ models. We first consider the dynamics of ionic solvation and then compare the dipolar solvation case. Finally, in Sec. IV we examine how the predictions of these inhomogeneous continuum models relate to results of time resolved fluorescence experiments and to recent molecular theories.

II. THEORETICAL

In this section we derive expressions for the time-dependent solvation response accompanying a step function jump of the charge on an ionic solute. We consider two related solvent models, one containing discrete shell regions of varying dielectric constant and the other consisting of a continuous, radially dependent dielectric function $\epsilon(r)$.

We first treat the discrete shell model and then generalize the results obtained to cover the continuous $\epsilon(r)$ case. The ionic solute, identical in the two models, is represented by a centered point charge of magnitude $q$ embedded in a spherical cavity of radius $r_0$ and dielectric constant $\epsilon_0$. The cavity dielectric constant $\epsilon_0$ actually plays no role in the energetics of ionic solvation in the linear response approach undertaken here (this is not true for dipolar solvation however) but it is retained throughout for the sake of generality. In the discrete shell model the solvent consist of a series of $n$ concentric shell regions, labeled by an index $j = 1,2,\ldots,n$. The $j$th region lies between inner and outer radii $r_{j-1}$ and $r_j$ and has a homogeneous dielectric constant $\epsilon_j$. An additional region, $j=n+1$, with dielectric constant $\epsilon_{n+1}$ equal to the bulk value $\epsilon_0$ extends from $r_n$ out to infinity.

The (static) free energy of solvation for such a system is easily obtained using continuum electrostatics.\textsuperscript{50} Consideration of Poisson’s equation for a spherically symmetric system shows that the electric potential in each homogeneous shell region, $\varphi_j$, is of the form

$$\varphi_j = A_j + B_j \frac{1}{r_j}, \quad j = 0,1,\ldots,n+1,$$

where $A_j$ and $B_j$ are constants independent of $r$. Application of the usual boundary conditions\textsuperscript{50}:

(i) $\varphi \to 0$ as $r \to \infty$,

(ii) $\varphi_j(r_j) = \varphi_{j+1}(r_j)$,

(iii) $\frac{\partial \varphi_j}{\partial r}(r_j) = \epsilon_j - \epsilon_{j+1} q + \frac{\epsilon_j}{\epsilon_{j+1}} q + 1$, \quad ($\varphi = \frac{\partial \varphi}{\partial r}$ and the fact that the only source term in region 0 is $q$, $\varphi_0=q/\epsilon_0$).

(iv) $B_0 = q/\epsilon_0$,

serve to determine the $A_j$ and $B_j$ and thus the potential in all regions. The result is

$$B_j = q/\epsilon_j, \quad j = 0,1,\ldots,n+1,$$  \hspace{1cm} (2.2a)

$$A_j = q \sum_{k=j}^{n} \frac{1}{r_k} \left( \frac{1}{\epsilon_{k+1}} - \frac{1}{\epsilon_k} \right), \quad j = 0,1,\ldots,n,$$  \hspace{1cm} (2.2b)

$$A_{n+1} = 0.$$  \hspace{1cm} (2.2b)

[In applying Eq. (2.2) to $j=0$, $\epsilon_0$ refers to the cavity dielectric constant $\epsilon_0$, and not the bulk value.] It is the constant part of the potential within the solute cavity $A_0$ that determines the solvation energy. This term can be written

$$A_0 = q \left[ \frac{1}{\epsilon_0 r_0} - \frac{1}{\epsilon_0 r_1} + \sum_{k=1}^{n} \frac{1}{\epsilon_k r_{k-1}} + \frac{1}{\epsilon_k r_k} \right].$$  \hspace{1cm} (2.3)

The free energy of solvation $E_{\text{solv}}$ depends on the reaction potential $\varphi_R$ via

$$E_{\text{solv}} = \frac{1}{2} q^2 \varphi_R$$  \hspace{1cm} (2.4)

with $\varphi_R$ being given by

$$\varphi_R = \varphi_0(\epsilon_j) - \varphi_0(\epsilon_1) = q \left[ A_0(\epsilon_j) - A_0(\epsilon_1) \right].$$  \hspace{1cm} (2.5)
In these expressions \( \varphi_R(\epsilon_j) \) and \( \varphi_g(\epsilon_j = 1) \), and the corresponding \( A_j \)'s, respectively, denote the potential \( r = 0 \) for a given set of solvent parameters \( \{ \epsilon_j, j = 1, 2, \ldots, n + 1 \} \) and the potential that would obtain when all solvent \( \epsilon_j \)'s are unity, i.e., when the solute is in vacuum. By combining Eqs. (2.3) and (2.5) the final result for the static reaction potential can be written:

\[
\varphi_R = -q \left[ \frac{1}{r_0} - \sum_{k=1}^{n+1} \frac{1}{\epsilon_k \left( \frac{1}{r_{k-1}} - \frac{1}{r_k} \right)} \right],
\]

where we let \( r_{n+1} \to \infty \) for notational convenience.

To incorporate dynamics into the solvation model we assume that the frequency dependent dielectric response of all solvent shells follow a common Debye law:

\[
\epsilon_j(\omega) = \epsilon_\infty + \frac{\epsilon_j - \epsilon_\infty}{1 + i\omega \tau_D}.
\]

An essential feature of the above expression is the use of a single \( \tau_D \) to describe all solvent regions. By virtue of this choice we are assuming that the solvent’s response to an external field has the same frequency dependence at all points despite the fact that the magnitude of the response depends on placement relative to the solute. That is, we assume that the frequency and spatial dependences of \( \epsilon(r, \omega) \) are separable such that

\[
\epsilon(r, \omega) - \epsilon_\infty = f(r)g(\omega).
\]

This same separation is also implicit in MSA treatments of solvation dynamics and, while clearly not exact, it provides a good first approximation. Given this form of \( \epsilon(\omega) \) and assuming a linear response we may then generalize the reaction potential to include nonzero frequencies by expressing \( \varphi_R \) as

\[
\varphi_R(\omega) = -q\omega \varphi_R(\omega)
\]

with

\[
r(\omega) = \frac{1}{r_0} - \sum_{k=1}^{n+1} \frac{1}{\epsilon_k \left( \frac{1}{r_{k-1}} - \frac{1}{r_k} \right)} = \frac{1}{r_0} \frac{1}{\epsilon_k(\omega)}.
\]

The frequency dependent function \( r(\omega) \) describes the reaction potential that would be seen by a fictitious solute whose charge \( q(\omega) \) varied sinusoidally in time at frequency \( \omega \). For an arbitrary time varying solute charge \( q(t) \) the free energy of solvation evolves according to

\[
E_{\text{solv}}(t) = \frac{1}{2} \int_{-\infty}^{t} r_p(t-t')q(t')dt',
\]

where the pulse response function \( r_p(t) \) is the inverse Laplace transform of \( r(\omega) \). For comparison to experimental studies of solvation dynamics we are interested in the energy relaxation \( \Delta E(t) \) that occurs after a step function jump of magnitude \( \Delta q \) in the solute charge. For a charge jump at \( t = 0 \), \( \Delta E(t) \) is given in terms of the step response function \( R(t) \) by

\[
\Delta E_{\text{solv}}(t) = -1/2(\Delta q)^2 R(t).
\]

This latter response function, normalized as in Eq. (1.1), is the quantity which is directly comparable to the experimentally observed Stokes shift response function \( C(t) \) [Eq. (1.6)]. \( R(t) \) is obtained from \( r(\omega) \) via

\[
R(t) = \int_{t'}^{\infty} \tilde{r}_p(t')dt',
\]

and

\[
\tilde{r}_p(t) \equiv \mathcal{L}^{-1}\{r(\omega) - r(\omega \to \infty)\},
\]

where \( \mathcal{L}^{-1} \) denotes an inverse Laplace transform. By subtracting the infinite frequency component from \( r(\omega) \), we remove from \( R(t) \) the instantaneous (and unobservable) part of the response that arises due to \( \epsilon_\infty \). Using Eq. (2.7) \( r(\omega) - r(\infty) \) can be written as

\[
r(\omega) - r(\infty) = \sum_{k=1}^{n+1} f_k \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_k(\omega)} \right).
\]

Substituting Eq. (2.7) for \( \epsilon(\omega) \) and rearranging this becomes

\[
r(\omega) - r(\infty) = \frac{1}{\epsilon_\infty \tau_D} \sum_{k=1}^{n+1} f_k \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_k} \right)
\]

\[
\times \left[ \frac{1}{\epsilon_\infty} \frac{1}{\tau_D} + i\omega \right]^{-1}.
\]

Since the terms in braces are Laplace transforms of exponentials, the final result for \( R(t) \) can be written analytically as

\[
R(t) = \sum_{k=1}^{n+1} R_k(t) = \sum_{k=1}^{n+1} a_k e^{-t/\tau_k},
\]

where

\[
a_k = \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_k} \right) \left( \frac{1}{\tau_{k-1}} - \frac{1}{\tau_k} \right)
\]

and

\[
\tau_k = \left( \frac{\epsilon_\infty}{\epsilon_k} \right) \tau_D.
\]

Equation (2.17) represents the final result for the discrete multishell model and an ionic solute. The result is fairly simple and intuitive. The dynamical response of a multishell solvent consists of a sum of independent responses, one from each distinct shell. The response time of a given shell \( k \) is just the longitudinal relaxation time \( (\epsilon_\infty/\epsilon_k) \tau_D \) associated with the dielectric constant of that shell. The relative contribution of a particular shell to the total response \( a_k \) is given by a product of a "dielectric strength" (\( \epsilon \)) term and an "effective size" (\( r \)) term as described by Eq. (2.17b).

The second solvent model to be considered is one in which the dielectric constant varies continuously as some function \( \epsilon(r) \) of distance from the solute. Results for this case can be easily derived from the above multishell model by viewing \( \epsilon(r) \) as the limit of a set \( \{ \epsilon_j \} \) of discrete shells as number of shells approaches infinity. In this limit \( \epsilon_k \to \epsilon(r_k) \to \epsilon(r) \) and the factor \((1/r_{k-1} - 1/r_k) \to d(1/r) = dr/r^2 \) so that the analog of Eq. (2.6) for the reaction potential can be written:

\[
\varphi_R = -q \left[ \frac{1}{r_0} - \int_{r_0}^{\infty} \frac{dr}{r^2 \epsilon(r)} \right].
\]
To obtain the time-dependent response we assume the continuous analog of Eq. (2.7):

$$\varepsilon(r, \omega) = \varepsilon_\infty + \frac{\varepsilon(r) - \varepsilon_\infty}{1 + i\omega\tau_p}.$$  

(2.19)

As long as \(\varepsilon(r)\) is a well behaved function, the steps leading to \(R(t)\) are identical to those given above for the multishell model except for replacement of the sum over shells by the integral over \(r\) and \(\varepsilon_n(\omega)\) by \(\varepsilon(r, \omega)\). The final result for the solvent step response function for the continuous \(\varepsilon(r)\) model is

$$R(t) = \int_0^\infty R_s(r,t)dr = \int_0^\infty a(r)e^{-\nu /\tau(r)}dr,$$  

(2.20a)

where

$$a(r) = \frac{1}{r^2} \left[ \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon(r)} \right]$$  

(2.20b)

and

$$\tau(r) = \frac{\varepsilon_\infty}{\varepsilon(r)}.$$  

(2.20c)

Just as above, the total solvent response consists of the superposition of independent responses from different solvent regions. In the present case there are an infinite number of "regions," i.e., distances from the solute. The total response now contains a continuous distribution of response times \(\tau(r)\) corresponding to the distribution of longitudinal times implied by a continuous \(\varepsilon(r)\).

We have also examined the dynamics of solvation of a dipolar solute with both of the above solvent models. The nature of solutions obtained in this case are very similar to those just described for an ionic solute. That is, different solvent regions contribute independently to the total response each with its characteristic response time determined by its local dielectric constant. For a point dipole the relevant time constants differ slightly from the longitudinal relaxation time \(\tau_p\) as described by Eq. (1.5). Unfortunately, due to the slightly more complicated form of the dipolar reaction field as compared to the ionic reaction potential we were not able to obtain simple analytical expressions for the time-dependent response in the dipole case. Instead, the \(R(t)\) functions had to be calculated by transforming the complex \(r(\omega)\) reaction field functions numerically. Details of how these calculations were carried out are provided in the Appendix.

III. RESULTS

The first solvent model we will consider is what we will refer to as the single shell model. The solute is pictured as consisting of two homogeneous regions: a first shell region of one solvent diameter in thickness that has a modified dielectric constant \(\varepsilon_1\), and a bulk solvent region having dielectric constant \(\varepsilon_B\). This model represents the simplest modification of the homogeneous continuum model that accounts for the fact that first shell solvent molecules are somehow different from bulk solvent. As already mentioned, such a single shell model is considerably better at correlating free energies of solvation than is the Born model itself, albeit with the addition of an adjustable parameter \(\varepsilon_1\).

The ionic solvation dynamics predicted with a single shell model are obtained by specializing the multishell formulas of Sec. II to the case \(n = 1\). Denoting the solute and solvent radii by \(r_s\) and \(r_n\), respectively, the outer radius of the nearest neighbor shell region is \(r_1 = r_s + 2r_n\), and the solvent response to a step change in solute charge is given by

$$R(t) = a_1e^{-\nu /\tau_1} + a_Be^{-\nu /\tau_B},$$  

(3.1)

with

$$a_1 = \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_1} \right) \left( \frac{1}{r_s} - \frac{1}{r_1} \right), \quad \tau_1 = \frac{\varepsilon_\infty}{\varepsilon_1} \tau_D,$$  

(3.2)

and

$$a_B = \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_B} \right) \frac{1}{\tau_B} = \frac{\varepsilon_\infty}{\varepsilon_B} \tau_D.$$  

(3.3)

In these expressions the static dielectric constants of the shell and bulk are \(\varepsilon_1\) and \(\varepsilon_B\), \(\varepsilon_\infty\) is the infinite frequency dielectric constant, and \(\tau_D\) the Debye relaxation time. As described by Eq. (2.7), \(\varepsilon_\infty\) and \(\tau_D\) are assumed to be the same for both regions. The predicted response function is biexponential and consists of separate contributions from the two solvent regions. The "bulk" region is responsible for the component that decays with the usual longitudinal relaxation time of the bulk solvent, \(\tau_B = \tau_L = (\varepsilon_\infty / \varepsilon_B) \tau_D\). This is the same time scale predicted by homogeneous continuum theories. The new feature that arises in the single shell case is a new relaxation time associated with the modified first shell dielectric constant \(\varepsilon_1\), given by \(\tau_1 = (\varepsilon_\infty / \varepsilon_1) \tau_D\).

To fully specify the model some choice must be made for the parameter \(\varepsilon_1\). Clearly we want \(\varepsilon_\infty\ll \varepsilon_1\ll \varepsilon_B\) but since \(\varepsilon_1\) is neither a true bulk nor molecular quantity there is no obvious choice to be made. Abraham and Liszt 36 found that a small value of \(\varepsilon_1 = 2\) gave good agreement between observed and calculated solvation free energies of univalent ions in several solvents. In order to be consistent with the continuous \(\varepsilon(r)\) calculations discussed below we will not take \(\varepsilon_1\) to be a constant but rather let it vary as some small fraction of \(\varepsilon_B\). Defining the fraction \(f_1\) by

$$f_1 = \frac{\varepsilon_1 - \varepsilon_\infty}{\varepsilon_B - \varepsilon_\infty},$$  

(3.4)

FIG. 1. \(S(t)\) response functions for ionic solvation calculated from the shell model with parameters \(\varepsilon_1/\varepsilon_\infty = 10, f_1 = 0.1,\) and \(\rho = 0.01-100\) as indicated.
we have chosen $f_1 = 0.1$ for our calculations. Such a value is in keeping with the choice of Abraham and Liszi and is also consistent with MSA predictions to be discussed later.

Figures 1–3 illustrate the way that the dynamics predicted by the single shell model vary with solvent/solute parameters. In comparing dynamics, we will henceforth use the normalized response function $S(t) = R(t)/R(0)$, defined by Eq. (1.1), rather than $R(t)$ itself. Figure 1 shows a set of such normalized $S(t)$ curves corresponding to $\epsilon_B/\epsilon_\infty = 10$ and $f_1 = 0.1$ for a series of values of the solvent to solute size ratio $\rho = r_i/r_0$. The two component time constants that arise with this set of parameters are $\tau_0 = \tau_L = 0.1 \tau_D$, the bulk longitudinal relaxation time, and the much longer time constant $\tau_1 = 0.56 \tau_D$, associated with relaxation of first shell solvent. For size ratios in the range $0.1 < \rho < 2$ the $S(t)$ response obtained by superposing contributions with these two decay times is noticeably nonexponential. Outside of this range the decays are reasonably well represented by a single exponential having one or the other of the component time constants. Here and throughout the subsequent discussion we will compare our results to the behavior expected for a homogeneous continuum solvent.

![Graph](image1)

**FIG. 2.** Normalized average response times $\langle \tau \rangle/\tau_L$ for ionic solvation calculated from the shell model as a function of solvent/solute size ratio $\rho$. Model parameters are $f_1 = 0.1$, $\epsilon_\infty = 1$, and $\epsilon_B = 2-100$ as indicated.

![Graph](image2)

**FIG. 3.** Normalized average response times $\langle \tau \rangle/\tau_L$ for ionic solvation calculated from the shell model as a function of solvent/solute size ratio $\rho$. Model parameters are $f_1 = 0.1$, and $\rho = 0.1-10$ as indicated.

Under the assumption of a Debye $\epsilon(\omega)$, this benchmark prediction is $S(t) = \exp(-t/\tau_D)$. One means of quantifying the deviation from homogeneous continuum behavior is through use of the average $S(t)$ time constant $\langle \tau \rangle$, defined by

$$\langle \tau \rangle = \int_0^\infty S(t)dt. \quad (3.5)$$

In Figs. 2 and 3 we plot the ratio $\langle \tau \rangle/\tau_L$ as a function of model parameters $\rho$ and $\epsilon_B/\epsilon_\infty$. It is interesting that the dependence on both $\rho$ and $\epsilon_B/\epsilon_\infty$ are functionally similar since the size ratio only influences the relative amplitudes, whereas $\epsilon_B/\epsilon_\infty$ mainly affects the exponential time constants (for fixed $f_1$). In the limits $\rho \to 0$ and $\epsilon_B/\epsilon_\infty \to 1$ the homogeneous continuum behavior is observed. For either $\rho$ or $\epsilon_B/\epsilon_\infty \to \infty$ the deviation of $\langle \tau \rangle$ from $\tau_L$ saturates at some finite value. The largest deviation that can be achieved by the single shell model is of course $\langle \tau \rangle = \tau_L = 1/f_1$.

We next consider the dynamics of ionic solvation for a continuum solvent whose dielectric constant is a smoothly varying function of distance from the solute. Like $\epsilon_i$, the function $\epsilon(r)$ has no precise definition in a real liquid so that the choice of a particular functional form for $\epsilon(r)$ is somewhat arbitrary. To explore what effect the form of $\epsilon(r)$ has on the dynamics we examined the set of functions listed in Table I. A number of these functions have previously been considered by Ehrenson with respect to the calculation of static solvent properties. All functions are defined such that $\epsilon(r_0) = \epsilon_i$ and $\epsilon(r \to \infty) = \epsilon_\infty$ and contain a single adjustable length scale parameter that determines the rapidity of approach to $\epsilon_B$. Several of the functions in Table I have some physical justification. For example, the power function in the case of $\rho = 4$ has been used by Buckingham to represent the effect that dielectric saturation has on the dielectric constant about an ion. The "inverse exponential" form was proposed by Kornyshev to represent the variation in dielectric constant that results from consideration of nonlocal dielectric effects using a simple model for $\epsilon(k)$. The remaining functions, however, have been chosen merely on the basis of their mathematical convenience.

![Table](image3)

**TABLE I.** $\epsilon(r)$ functions examined.

<table>
<thead>
<tr>
<th>No. designation</th>
<th>$\epsilon(\rho)$ ($\rho = r/r_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Single shell</td>
<td>$\epsilon_i$ for $\rho &lt; (\tau_1 - 1)/2$</td>
</tr>
<tr>
<td>2 Exponential</td>
<td>$\epsilon_B - (\epsilon_B - \epsilon_i)\exp\left[-(\rho - 1)/\lambda\right]$</td>
</tr>
<tr>
<td>3 Inverse exponential</td>
<td>$\epsilon_1 \cdot \epsilon_B - (\epsilon_B - \epsilon_i)\exp\left[-(\rho - 1)/\lambda\right]^{-1}$</td>
</tr>
<tr>
<td>4 Power</td>
<td>$\epsilon_B - (\epsilon_B - \epsilon_i)\rho^{-\gamma}$</td>
</tr>
<tr>
<td>5 Hyperbolic tangent</td>
<td>$\epsilon_B - (\epsilon_B - \epsilon_i)\tanh\left[(\rho - 1)/\lambda\right]$</td>
</tr>
</tbody>
</table>

Figure 4 compares the $\epsilon(r)$ dependence of the various functions studied including that of the shell model discussed previously. In order to compare these functions at corresponding values of their length scale parameters we have taken the point at which the fraction $f(r)$,

$$f(r) = \frac{\epsilon(r) - \epsilon_i}{\epsilon_B - \epsilon_i}, \quad (3.6)$$

achieved \( r_{1/2} = 1/2 \) for some common value of \( r_{1/2} \). In Fig. 4 we have picked \( \lambda \) of the exponential function (2) was arbitrarily set to unity which fixes \( r_{1/2} \) to be 1.69\( r_0 \). The length scale parameters of the remaining functions are chosen such that all exponential functions are given in the captions to Figs. 4 and 5.) As can be seen from Fig. 4, one important difference between the four continuous \( \epsilon(r) \) functions is their behavior at large \( r \). The approach to \( \epsilon_s \) is most rapid for the inverse exponential function and becomes progressively slower in the order \( \exp^{-1} > \tanh > \exp > r^{-p} \). We also note that the inverse exponential function is somewhat unique within this set since it is the only function that has zero slope at the \( \rho = 1 \) limit.

The dynamics associated with these various \( \epsilon(r) \) functions are illustrated in Fig. 5. The response functions shown here and in the following sections were obtained by numerical integration of Eq. (2.20). We assume throughout that \( \epsilon_n \), the value of the solvent dielectric constant at the solute boundary, is equal to the background, infinite frequency value \( \epsilon_\infty \) that arises from the nonorientational polarizability of the solvent. Aside from the choice of the \( \epsilon(r) \) function the dynamics then depend on only two parameters, the length scale parameter and the ratio \( \epsilon_s / \epsilon_\infty \).

Figure 5 compares the effect that the functional shape has on the calculated \( S(t) \) curves for \( \epsilon_s / \epsilon_\infty = 50 \) and \( \lambda_{\infty} = 5 \). We will discuss the dependence on these model parameters shortly. As can be seen from Fig. 5, all of the \( \epsilon(r) \) functions yield significantly non-exponential \( S(t) \) responses. The different \( \epsilon(r) \) functions are quantitatively different, displaying values of \( \langle r \rangle_{\tau_L} \) that range between 5–11 (see caption). These differences are easily rationalized on the basis of the relative ordering of the \( \epsilon(r) \) near to the solute (Fig. 4). There are also qualitative differences between the \( S(t) \) curves. The distinctly biexponential decay predicted from the shell model is quite different from the behavior calculated from all of the continuous \( \epsilon(r) \) models. Further, the shapes of the \( S(t) \) curves differ significantly depending on the choice of \( \epsilon(r) \) functionality. Where

as an appropriate rescaling of length parameters among these \( \epsilon(r) \) choices can lead to agreement in their average response times, the detailed time dependence of the responses remain distinct, at least in situations where the departure from \( \tau_L \) is large.

In order to simplify the discussion we will consider in more detail only two of the \( \epsilon(r) \) functions listed in Table I—the exponential and inverse exponential functions. The exponential function is perhaps the most desirable among the \( \epsilon(r) \) choices by virtue of its independent linear distance scaling with \( \lambda \) and simple form. The inverse exponential function is somewhat more complicated because the length scale and shape of the \( \epsilon(r) \) curve depends slightly on \( \epsilon_s / \epsilon_\infty \). As will be discussed later the inverse exponential function yields the most satisfactory agreement with the MSA model and with experimental results. We consider both \( \epsilon(r) \) models here in order that the differences in their dynamics may serve to represent the range of behavior available from continuous models in general.

Figure 6 illustrates the way in which \( \epsilon(r) \) and the derived quantity \( a(r) \) [Eq. (2.20)] vary with \( \lambda \) for the exponential model. As in the discrete shell model, the \( S(t) \) response is decomposable into a sum of contributions from different solvent regions. Now however, the regions are continuously distributed according to \( r \). The distribution of relaxation times \( \tau \) follows the inverse of \( \epsilon(r) \) [Eq. (2.20)] and contains all values between \( \tau_D \) at \( r = r_0 \) to the bulk longitudinal relaxation time \( \tau_L \) achieved in the limit \( r \to \infty \). The way in which these times are manifest in the \( S(t) \) decay depends on the weighting function \( a(r) \) [Fig. 6 (b)]. Figure 7 shows the influence of \( \lambda \) on the dynamics for two choices of \( \epsilon_s / \epsilon_\infty \). For small \( \lambda \), the response is nearly exponential over several decay times, and has an average time constant only slightly larger than \( \tau_L \). At the other extreme of large \( \lambda \), \( a(r) \) is large in regions where \( \tau(r) \) is close to \( \tau_D \). In this case time
constants over the entire $\tau_D$ to $\tau_L$ range have significant weight and the resultant solvation response is highly nonexponential in character. Comparing Figs. 7(a) and 7(b) we note that increasing $\varepsilon_B/\varepsilon_\infty$ has a similar effect on the $S(t)$ decay to that of increasing $\lambda$. Thus, although the shapes of the $\varepsilon(r)$, $a(r)$, and $\tau(r)$ curves are unchanged from those of Fig. 6 when $\varepsilon_B/\varepsilon_\infty$ is increased to 50, because $\tau_L$ is five times faster in this case the distribution of relaxation times represented in the response becomes broader.

Figures 8 and 9 show the corresponding $\varepsilon(r)$, $a(r)$, and resulting $S(t)$ curves for the case of the inverse exponential model. Nearly all of the above discussion for the exponential model holds equally well for the inverse exponential $\varepsilon(r)$ function. One exception is that here the rapidity with which $\varepsilon(r)$ approaches $\varepsilon_B/\varepsilon_\infty$ is partially dependent on $\varepsilon_B/\varepsilon_\infty$. Thus for $\lambda = 1$ the value of $r$ for which $f(r) = 1/2$ is $3.4\alpha_0$ for $\varepsilon_B/\varepsilon_\infty = 10$ vs $4.9\alpha_0$ for $\varepsilon_B/\varepsilon_\infty = 50$. The shapes of the $\varepsilon(r)$, $a(r)$, and $\tau(r)$ curves do therefore depend somewhat on $\varepsilon_B/\varepsilon_\infty$. The distribution of relaxation times broadens with increased $\varepsilon_B/\varepsilon_\infty$ both because of this effect and because the range between $\tau_D$ and $\tau_L$ increases.

Figures 10 and 11 summarize how the characteristics of the $S(t)$ response functions vary with the model parameters $\lambda$ and $\varepsilon_B/\varepsilon_\infty$. The data in these plots were generated from...
least squares fits of the calculated $S(t)$ decays to both biexponential,

$$S(t) = a_1 e^{-(t/\tau)} + a_2 e^{-(t/\tau)}$$

and stretched exponential,

$$S(t) = e^{-(t/\tau)^\alpha}$$

forms. We have found that in regimes of small $\lambda$ and/or $\epsilon_B/\epsilon_\infty$ the four parameter, biexponential fit is usually superior, whereas in the opposite extreme the two parameter, stretched exponential fit is often preferable. We note however that the $S(t)$ curves do not exactly fit either of these two forms over most of the model parameter space. In principle the $S(t)$ decays should not be biexponential since a distribution of relaxation times are present. There is also little reason to expect that they should be of a stretched exponential form either since, while such a form does arise from the presence of distributed relaxation times, only certain sorts of distributions yield this functionality.\(^{31}\) For our purposes this fitting simply aids in quantifying the $S(t)$ curves by allowing for the analytic calculation of average decay times $\langle \tau \rangle$ from the fitted parameters. We further use the stretched exponential parameter $\alpha$ as a gauge of the nonexponential character of the response.

The results in Figs. 10 and 11 display the predictions of the two $\epsilon(r)$ models over ranges of the model parameters relevant for comparison to experiment. Choice of a "relevant" range for $\lambda$ is based upon assuming solvent/solute size ratios between 0.1–10 requiring that a physically reasonable $\epsilon(r)$ reach $f(r)$ = 0.9 within 2–4 solvent shells from the solute. Values of $\lambda$ between 0.1–10 roughly cover this range for both $\epsilon(r)$ functions. The behavior as a function of $\lambda$, illustrated in Fig. 10 is qualitatively similar in the two $\epsilon(r)$ models. When larger values of $\lambda$ are considered, the $\langle \tau \rangle/\tau_L$ vs log ($\lambda$) curves also exhibit the same sigmoidal shape and saturation at high $\lambda$ that was observed for the single shell model ($\lambda \rightarrow \rho$, Fig. 2). Several important differences between the characteristics of the $S(t)$ response functions produced by the two $\epsilon(r)$ models are also evident from these figures. Since such differences influence our comparisons with the MSA model and experimental results we discuss them in some detail. The most important difference lies in the degree to which the dynamics deviate from homogeneous continuum [i.e., $\exp(-t/\tau_L)$] behavior. In order to compare roughly equivalent values of $\lambda$ in the two cases we assume equal solute and solvent sizes ($\rho = 1$) and require that both functions attain $f(r)$ = 90% after two solvent shells ($r = 5r_0$). The length scale parameters for such a situation are $\lambda_{\text{exp}} = 1.75$ and $\lambda_{\text{inv}} = 0.65$ for $\epsilon_B/\epsilon_\infty = 50$. The ratio $\langle \tau \rangle/\tau_L$ for $\epsilon_B/\epsilon_\infty = 50$ is then $\sim 3.7$ for the exponential model and $\sim 9$ for the inverse exponential model. Thus, for comparable parameters the inverse exponential function produces much larger deviations from $\tau_L$ than does the exponential function. The response functions produced by the inverse exponential model also tend to contain a broader distribution of relaxation times as judged by the generally lower values we observe for the stretched exponential exponents $\alpha$ [Eq. (3.8), Fig. 11(b)] in the two cases. The fact that the inverse exponential function approaches $\tau_0$ with zero slope allows more time constants near $\tau_D$ to be effectively sampled (see Figs. 6 and 8) producing a longer average time constant and a larger value of $\alpha$. A final difference between the behavior predicted by the two models is the dependence of $\langle \tau \rangle/\tau_L$ on $\epsilon_B/\epsilon_\infty$ illustrated for the inverse exponential function in Fig. 11(a). Unlike the shell model, for which $\langle \tau \rangle/\tau_L$ was limited by the choice of $f_n$, neither continuous $\epsilon(r)$ model has a strict limit as $\epsilon_B/\epsilon_\infty$ gets large. Nonetheless, the exponential model (not shown but see Fig. 13)
increases only rather slowly, having a roughly logarithmic dependence on \( \epsilon_B / \epsilon_\infty \) for large values of this parameter. For the inverse exponential function, in contrast, Fig. 11(a) shows that there appears to be a linear relationship between \( \langle \tau \rangle / \tau_L \) and \( \epsilon_B / \epsilon_\infty \) such that

\[
\frac{\langle \tau \rangle}{\tau_L} = F(\lambda) \left( \frac{\epsilon_0}{\epsilon_\infty} - 1 \right),
\]

(3.9)

where \( F(\lambda) \) is some function describing the shapes of the curves in Fig. 10(b). (It is not obvious why such a simple relationship should hold in this case.) This last difference between the two functions arises mainly because of the effective increase of the \( \epsilon(r) \) length scale with increasing \( \epsilon_B / \epsilon_\infty \) that occurs with the inverse function but not with the exponential function.

All of the above discussion has concerned the dynamics of ionic solvation. A final aspect of these models that we now consider is how the predicted dynamics are changed when the solute interacts with the solvent via a point dipole rather than a point charge. In the case of homogeneous continuum models the difference in dynamics is trivial. Whereas the dipolar and ionic cases can be brought into fairly close agreement in all respects through an overall scaling of the solvent length scale parameter. We illustrate this point in Figs. 13 and 14 which are for the exponential \( \epsilon(r) \) solvent model. In Fig. 13 we show how \( \langle \tau \rangle / \tau \) varies with \( \epsilon_B / \epsilon_\infty \) for a dipolar solute (solid curves) at several values of \( \lambda \). First we note that compared to the equivalent ionic data, the deviation from homogeneous continuum predictions is approximately twice as large for the dipole. By a single relative scaling, \( \lambda_{ion} = 2.99 \lambda_{dipole} \), however, the dipole and ion (dashed) curves can be made to nearly coincide.

Figure 14 shows how the \( S(t) \) functions of the exponential \( \epsilon(r) \) model compare under this same scaling. While the curves are similar, they do differ in that dipole response is more nearly exponential than is the ionic response at the scaled \( \lambda \). These similarities and differences between solvation dynamics predicted for an ion vs a dipole are readily understood in terms of the different ranges of interaction.
that the ion and dipole have with the solvent. For a homogeneous continuum solvent the total interaction energy between an ion and a shell of solvent at a radius \(r\) is proportional to \(r^{-2}\), whereas the analogous energy in the dipole case varies as \(r^{-6}\). Thus the interaction is of much shorter range for the dipole and it therefore effectively senses only a fraction of the solvent region probed by ion. By scaling up the length parameter in the ionic case one can force the two solutes to sample the same part of the \(\varepsilon(r)\) distribution and thus show similar dynamics. The correspondence is not exact however since the functional dependence of energy on distance, i.e., the \(a(r)\) function of Eq. (2.20b), still differs in the two cases.

**IV. DISCUSSION**

In the preceding section we examined the dynamical solvation response predicted on the basis of several inhomogeneous continuum models. The models all consist of a spherical solute having either a centered point charge or point dipole that is surrounded by a continuum fluid whose static dielectric constant is some function of distance from the solute. The frequency and spatial dependence of the di-electric constant are assumed to be separable with the frequency dependence being given by a Debye form, \(\varepsilon(r, \omega) - \varepsilon_\infty = (\varepsilon(r) - \varepsilon_\infty) / (1 + i\omega\tau_D)\), where \(\tau_D\) is the Debye relaxation time of the bulk solvent. The main results obtained with such models can be summarized as follows:

(i) Invoking solvent regions in which the dielectric constant differs from its bulk value introduces additional relaxation times in the response compared to homogeneous models. The new times that arise are simply the longitudinal relaxation times appropriate to the new dielectric constants introduced. Since we consider only models in which \(\varepsilon(r) < \varepsilon_\infty\), the additional response times are all longer than the bulk longitudinal relaxation time, and thus serve to slow the total response relative to homogeneous continuum models.

(ii) Single shell models that divide the solvent into two homogeneous regions give rise to biexponential \(S(t)\) functions, whereas models for which \(\varepsilon(r)\) is a continuous function of \(r\) produce a continuous distribution of relaxation times. Under the assumption that the dielectric constant at the solute boundary is equal to \(\varepsilon_\infty\) the relaxation times produced span the entire range between \(\tau_D\) and \(\tau_L\).

(iii) Since \(\varepsilon(r)\) is a spatially local function, the total solvation response can be broken down into a sum of independent contributions from different solvent regions. The contribution from solvent at a radius \(r\) has an exponential time dependence with time constant \(\tau = (\varepsilon_\infty / \varepsilon(r)) \tau_D\) (or \((2\varepsilon_\infty + 1) / [2\varepsilon(r) + 1]\) \(\tau_D\) for a dipolar solute). Assuming that \(\varepsilon(r)\) is a monotonically increasing function of \(r\), this means that the solvent response is slowest at the solute and becomes more rapid with increasing distance away.

(iv) The ratio \(\tau / \tau_L\), which is used to gauge deviations from homogeneous continuum behavior, increases monotonically with both the ratio \(\varepsilon_p / \varepsilon_\infty\) and the length scale parameter \(\rho\) or \(\lambda\) for all models studied.

(v) Quantitative features of the solvation response predicted from a continuous \(\varepsilon(r)\) model depend on the functional form chosen for \(\varepsilon(r)\). The shapes of the \(S(t)\) decays as well as \(\tau / \tau_L\) and its dependence on \(\varepsilon_p / \varepsilon_\infty\) change with \(\varepsilon(r)\) functionality.

(vi) For a given solvent model, solvation of a point dipole solute is slower than for an ion. The difference is a result of the shorter range of the dipole field compared to the ion field. Much of the difference between the ion and dipole cases can be accounted for through a simple rescaling of the solvent length parameter.

We now consider these results in light of a recent molecular model of ionic solvation dynamics and experimental time resolved fluorescence data. The molecular theory proposed by Wolynes \(^{24}\) and further developed by Rips et al. \(^{25}\) and Nichols and Calef \(^{26}\) extends the MSA treatment of the static structure about an ion in a dipolar hard sphere solvent \(^{24}\) to model the dynamics of ionic solvation. The essential feature of this theory that sets it apart from continuum theories is the use of a dipolar hard sphere model solvent in the MSA to determine a relationship between the equilibrium solvation energy of an ion and the solvent’s dielectric constant and size. Whereas we obtain the static reaction potential resulting from a continuum solvent model \(\varepsilon(r)\), the analogous quantity is obtained in the MSA treatment from a purely molecular, albeit crude, description of the solvent. The dynamics are introduced into the MSA model in the same way as they are in the present theory—by assuming that the relationship between the solvation energy and the static dielectric constant can be generalized to nonzero frequencies by replacing \(\varepsilon(\omega = 0)\) with a Debye type \(\varepsilon(\omega)\).

Predictions of the MSA model depend on three parameters \(\varepsilon_\infty\), \(\varepsilon_p/\varepsilon_\infty\), and the solvent/solute size ratio \(\rho\) as detailed in Refs. 25 and 35. The time dependence predicted by this model and its variation with these parameters is similar to that described for the continuous \(\varepsilon(r)\) models. The response is nonexponential and slower than \(\tau_L\), with the deviation \(\tau / \tau_L\) increasing with increasing \(\rho\), \(\varepsilon_p/\varepsilon_\infty\), and \(\varepsilon_\infty\). There are two primary differences between the predictions of the MSA model and ours. First, the parameter \(\varepsilon_\infty\) influences the MSA predictions in a substantial way, whereas only the ratio \(\varepsilon_p/\varepsilon_\infty\) is relevant in the continuum models. A second difference lies in how the two types of model behave in the limit of large solvent/solute size ratio \(\rho\) or \(\lambda\). [The size ratio is explicitly considered in the single shell model as determining the thickness of the first shell. It is implicit in the continuum models in the sense that to maintain the same solvent \(\varepsilon(r)\) behavior, a change in the solute size by a factor \(\alpha\) implies a change in \(\lambda\) to \(\lambda / \alpha\). Thus, \(\rho \propto \lambda\).] In the shell model, as the shell thickness increases a limiting time constant of \((\varepsilon_p/\varepsilon_\infty)\tau_D\) is reached. For the continuous \(\varepsilon(r)\) models, under the assumption that \(\varepsilon(0) = \varepsilon_\infty\), the limiting time approached in the large \(\lambda\) limit is \(\tau_D\) itself. Further, in both inhomogeneous continuum models the \(S(t)\) response becomes exponential in this limit. For the MSA model, on the other hand, as \(\rho \rightarrow \infty\) the response remains highly nonexponential and the limiting average decay time is typically in the range \(\tau_D/5 - \tau_D/2\), depending on parameters \(^{25,35}\). This latter time scale reflects single molecule dynamics and it differs from \(\tau_D\) to the extent that motions of neighboring solvent molecules are correlated.
Because the response closest to the solute is most important for determining deviations from homogeneous continuum behavior we will compare experimental results to the dynamics calculated for the ionic case. The actual situation is probably best described by something intermediate between the point charge and point dipole cases. Since we are only interested in a semiquantitative comparison the ionic choice is sufficient.

In Fig. 16 we plot \( \langle \tau \rangle / \tau_L \) vs \( \varepsilon_B / \varepsilon_\infty \) using data collected from a number of different experimental studies. As discussed in Sec. I, these data include results from a variety of different probe solutes and solvent types. Although there is considerable scatter in the data, a roughly linear correlation between the observed \( \langle \tau \rangle / \tau_L \) ratio and \( \varepsilon_B / \varepsilon_\infty \) is evident. Such a correlation implies that, more important than the differences among the various solute/solvent combinations studied, there is a single underlying cause for the deviation from the \( \tau_L \) expectation that is similar in all cases. That this underlying mechanism can be well represented by a single inhomogeneous continuum model for all solvents is shown by the solid line in Fig. 16, which is the result of the (ionic) inverse exponential model using a value of \( \lambda = 1.83 \). Figure 17 illustrates that the same value of \( \lambda \) also produces \( S(t) \) response functions that are in good agreement with the time dependence of the experimentally observed \( C(t) \) functions. Note that the model yields the correct time dependence over the wide range of dielectric constant \( \varepsilon_B / \varepsilon_\infty \sim 80-300 \) represented by the solvents and temperatures shown in Fig. 17. It is also worth pointing out that the ability to tune \( \lambda \) allows this continuum model to achieve much better agreement with experiment than is obtained with the dynamical MSA model. Fixing \( \rho \) to values appropriate to the overall solvent/solute dimensions, the latter model predicts values of \( \langle \tau \rangle / \tau_L \) that are much smaller than experimentally observed in solvents with high \( \varepsilon_B / \varepsilon_\infty \) ratio. In addition, the apparent linear dependence of \( \langle \tau \rangle / \tau_L \) on \( \varepsilon_B / \varepsilon_\infty \) is better fit by the inverse exponential \( \varepsilon(r) \) model than by the MSA model. This ability to mimic the experimental data is somewhat specific to the inverse exponential form of \( \varepsilon(r) \) and cannot be...
achieved for arbitrary inhomogeneous models. For example, the single shell model is inadequate to explain the nonexponential character of the observed C(t) decays. No such problem exists for the exponential \( \epsilon(r) \) model; however, this continuous model suffers similar difficulties in fitting the experimental data for acceptable parameters as does the MSA model. Although we do not wish to attach any particular significance to the inverse exponential form, we note that the value of \( \lambda = 1.83 \) needed to fit experiment produces an \( \epsilon(r) \) function that appears physically reasonable. As can be seen from Fig. 8(a), for this \( \lambda \), \( \epsilon(r) \) reaches 90% of \( \epsilon_0 \) by \( r/r_0 = 11 \), or assuming equal solute and solvent radii, after five solvent shells. A perturbed solvent region extending for five solvation shells might seem somewhat large, however, if we had considered the dipolar solute/inverse exponential model, similarly good agreement to experiment could be obtained for \( \lambda = 0.6 \) and a much smaller perturbed region. As already stated, we feel the best treatment of the solute is probably intermediate between the ionic and dipole cases and would lead to a more realistic \( \epsilon(r) \).

In conclusion, we have studied the dynamical predictions of several inhomogeneous continuum solvent models for both ionic and dipolar solute. Given a phenomenological \( \epsilon(r) \) as input, such models lead to simple, physically appealing solutions in terms of the superposition of responses from different solvent regions. In the ionic case, discrete shell models afford analytic results, while for arbitrary continuous \( \epsilon(r) \) results can be calculated from a trivial numerical integration. Through choice of suitable \( \epsilon(r) \) function it is possible fit experimental data more closely than can be accomplished with other currently available theories. Freedom in choosing an \( \epsilon(r) \), an asset in explaining experimental observations, is also the main weakness of our approach. Although such a phenomenological function can be used to mimic molecular effects, there is no rigorous justification for any particular form of \( \epsilon(r) \). A truly satisfactory understanding of the dynamics of solvation will, of course, ultimately depend on coming to terms with the molecular level details of the solvation process. In the future, more accurate molecular models will undoubtedly be developed that will bring us closer to such an understanding. However, since these models are likely to be quite complex, caricaturing their molecular features with effective \( \epsilon(r) \) functions may still prove to be an economical way of representing the behavior of real solvent/solute systems.

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APPENDIX

In this Appendix we outline the methods used to obtain solutions to the two solvent models described in Sec. II for the case of a dipolar solute. Here the solute is a spherical cavity of radius \( r_0 \) filled with dielectric medium of constant \( \epsilon_s \) and possessing a centered point dipole of magnitude \( \mu \). The energy of solvation of a dipole \( \mu(t) \) that is changing with time is given by

\[
E_{\text{sol}}(t) = -1/2 \mu(t) \cdot F_R(t),
\]

where \( F_R(t) \) is the reaction field at time \( t \). Assuming a linear response, \( F_R(t) \) can be expressed in terms of a pulse response function \( r_p(t) \) as

\[
F_R(t) = \int_{-\infty}^{t} r_p(t-t') \mu(t') dt'.
\]

The response function of interest is the function that describes the solvation response to a step function change in the solute dipole moment. This latter response function, which we denote \( R(t) \), is related to a frequency dependent reaction field factor \( r(\omega) \), via the relations (see Sec. II)

\[
R(t) = \int_{-\infty}^{\infty} \tau_p(t') dt',
\]

\[
\tau_p(t) = \mathcal{L}^{-1}_{\omega} \{ r(\omega) - r(\infty) \},
\]

where \( \mathcal{L}^{-1}_{\omega} \) denotes an inverse Laplace transformation. Physically, \( r(\omega) \) is the reaction field produced by a sinusoidally varying solute dipole of unit magnitude. As in Sec. II, we are not interested in that part of the \( R(t) \) response which is instantaneous, and we thus remove the infinite frequency contribution from \( r(\omega) \) in the definition of \( R(t) \). \( r(\omega) \) is obtained through a generalization of the static reaction field produced by a given \( \epsilon(r) \) dependence to include nonzero frequencies. Effectively this amounts to first solving the electrostatic problem to obtain the reaction field as a function of \( \epsilon(r) \) and then substituting \( \epsilon(r,\omega) \) for \( \epsilon(r) \) in the result to obtain \( r(\omega) \). As in the ionic case we assume that the \( r \) and \( \omega \) dependences of \( \epsilon(r,\omega) \) separate and that the frequency dependence is Debye like as described by Eq. (2.19).
Since the $r(\omega)$ that result in the dipole case are complicated functions, the desired $R(t)$ functions are obtained by performing the inverse Laplace transform and integration of Eqs. (A3) and (A4) numerically.

We first consider the multishell solvent model using the same notation as in Sec. II. The solution to the Laplace equation appropriate to dipolar symmetry is

$$q_j = \left( A_j r + B_j \frac{1}{r^3} \cos \Theta \right)$$

which holds for each homogeneous solvent region $j = 1$ to $n + 1$. The angle $\theta = 0$ defines the dipole direction. The boundary conditions are again:

(i) $q = 0$ as $r \to \infty$,
(ii) $q_j(\rho_j) = q_{j+1}(\rho_j),$
(iii) $q_j(\rho_j) = q_{j+1}(\rho_j),$

but now a dipolar source term applies, which changes condition (iv) to

(iv') $B_0 = \mu / \varepsilon_c$.

For these boundary conditions the $A_j$ and $B_j$ terms that determine the potential in each region can be expressed recursively as:

$$A_j = a_j A_{j+1} + b_j B_{j+1},$$

$$B_0 = \left( \frac{2 \mu}{\varepsilon_c} \right) \left[ \frac{(2 + f_0)(1 - f_j) + (1 - f_j)(1 + 2 f_j)(r_j/r_0)^3}{2(1 - f_0)(1 - f_j) + (1 + 2 f_0)(1 + 2 f_j)(r_j/r_0)^3} \right] \mu.$$  

The frequency dependent reaction field factor $r(\omega)$ is obtained from $F_{R}/\mu$ by substituting $\varepsilon_c(\omega)$ in Eq. (A7) for $\varepsilon_c$. The desired solvation response function $R(t)$ for this single shell model can then finally be obtained numerically via Eqs. (A3) and (A4). We used the numerical inverse Laplace transform method of Stehfest

$$F_{R} = [A_0(\varepsilon) - A_0(\varepsilon_c, \varepsilon_c = \varepsilon_b = 1)] \mu.$$  

The frequency dependent reaction field factor $r(\omega)$ is obtained from $F_{R}/\mu$ by substituting $\varepsilon_c(\omega)$ in Eq. (A7) for $\varepsilon_c$. The desired solvation response function $R(t)$ for this single shell model can then finally be obtained numerically via Eqs. (A3) and (A4). We used the numerical inverse Laplace transform method of Stehfest to carry out these calculations.

We now turn to the case of a continuous $\varepsilon(r)$. In Sec. II we obtained the reaction potential of an ionic solute for a continuous $\varepsilon(r)$ function by taking the appropriate limit of the results for the multishell model. Here, since the multishell results are not simple we take a different approach and begin directly with the Laplace equation,

$$\nabla \cdot [\varepsilon(r) \nabla \varphi(r)] = 0,$$

which for dipolar symmetry may be written

$$\frac{\partial}{\partial r} \left[ r^2 \varepsilon(r) \frac{\partial \varphi}{\partial r} \right] + \frac{\varepsilon(r)}{\sin \Theta} \frac{\partial}{\partial \Theta} \left[ \sin \Theta \frac{\partial \varphi}{\partial \Theta} \right] = 0.$$  

The dielectric inside the solute is homogeneous with $\varepsilon(r) = \varepsilon_c$ and the potential, $\varphi_0$, is simply

$$\varphi_0 = \left( A_0 + \frac{\mu}{\varepsilon_c} \frac{1}{r} \right) \cos \Theta.$$  

The $A_0$ term represents the homogeneous reaction field inside of the solute and it is this constant we wish to calculate. To obtain $A_0$, Eq. (A10) must be solved for the potential outside of the cavity. We follow an approach due to Debye and begin by separating the $\theta$ dependence by letting

$$\varphi_1 = (r, \Theta) = f(r) \cos \Theta,$$

where $f(r)$ now satisfies the radial equation:

$$\frac{d}{dr} \left( r \frac{d}{dr} \frac{df}{dr} \right) - 2\varepsilon(r)f(r) = 0.$$  

Application of the boundary conditions (i)–(iii) provides the following constraints on $f(r)$:

$$f(r) \to B_0 \frac{1}{r} \text{ as } r \to \infty,$$

$$A_0 \varepsilon_0 + \frac{\mu}{\varepsilon_c} \frac{1}{r_0} = f(r_0),$$

$$\varepsilon_c \left( A_0 - \frac{\mu}{\varepsilon_c} \frac{1}{r_0} \right) = \varepsilon(r_0) \left( \frac{df}{dr} \right)_{r_0}.$$  

The set of equations (A13)–(A16) must be solved numerically to obtain $f(r)$ and $A_0$. One begins at a large enough $r$.
such that \( \epsilon(r) \approx \epsilon_0 \) in which case \( f(r) \) is given by \( r^{-2} \) to within a constant \( B_1 \). Equation (A13) for \( f(r) \) is then numerically integrated from this point inward until the solute radius \( r = r_0 \) is reached. The two conditions (A15) and (A16) then serve to determine the unknown constant \( B_1 \) and the desired reaction field term \( A_0 \).

The dynamics are obtained from the above static analysis by generalizing \( \epsilon(r) \rightarrow \epsilon(r, \omega) \), \( f(r) \rightarrow f(r, \omega) \), \( \mu \rightarrow \mu(\omega) \), \( A_0 \rightarrow A_0(\omega) \), and \( B_1 \rightarrow B_1(\omega) \). Equations (A13)–(A16) then serve to determine the unknown constant \( B_1 \) and \( A_0(\omega) / \mu(\omega) \) for the particular frequency \( \omega \). Iterating through a range of frequencies between \( \pm 4096 \mathcal{R}_0^2 \) in this manner mapped out the full \( r(\omega) \) response (200 points) which was then converted to the desired final result, \( R(t) \), via Fourier transformation and subsequent integration according to Eqs. (A4) and (A3).

1See, for example, C. Reichardt, Solvent Effects in Organic Chemistry (Verlag Chemie, New York, 1979).


29See, for example, N. Mataga and T. Kubota, Molecular Interactions and Electronic Spectra (Dekker, New York, 1970), Chap. 8, for a review of the use of such models in spectroscopy.

30S. Brawner, Relaxation in Viscous Liquids and Glasses (American Ceramic Society, Columbus, 1985).


45See, for example, A. Geiger, Ber. Bunsenges. Phys. Chem. 85, 52 (1981), and references therein.

46P. Debye, Polar Molecules (Chemical Catalog Co., 1929), Chap. 6.


50See, for example, Ref. 49, Chap. 2; M. Fröhlich, Theory of Dielectrics (Oxford University, Oxford, 1958). Appendix A-2.


