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Gaussian Field Model of Dielectric Solvation Dynamics

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Extending the Gaussian model of solvation (Chandler, D. *Phys. Rev. E* **1993**, *48*, 2898) to dynamics, we focus specifically on the problem of dielectric relaxation. In the Gaussian model, the solvent is described in terms of a linear responding field that is expelled from the volume occupied by the solute. The excluded volume affects the normal modes of the system, thereby playing a significant role in solvation dynamics. Even in the context of dielectric continuum theory, the excluded volume affects the polarization response outside that volume. We show that this effect can be analyzed generally and analytically.

I. Introduction

Many chemical reactions in solution involve a rearrangement of the charge in the reactants. The time-dependent response of the solvent molecules to this change influences reaction dynamics. When that solute charge distribution is suddenly changed by light absorption to an excited electronic state of the solute, the latter is generally not in equilibrium with the solvent. The sudden change of solute charge distribution forces the solvent to rearrange to a state in equilibrium with the new solute charge distribution. The question that arises is how this relaxation process can be described microscopically in terms of the solvent−solute molecular interactions.

With the advent of ultrafast laser techniques, it is now possible to probe this detailed solvent relaxation dynamics. The experimental results, combined with the developments of theoretical models and computer simulations, have led to an appreciation of the importance of microscopic features on these processes.[1] Of particular importance is the effect of molecular size—the spatial correlations of the solvent in the vicinity of the solute. The dynamical mean spherical approximation (MSA)[2] as applied by Wolynes and others[3] was the first and most influential of theories to address this issue in solvation dynamics. Other approaches have been devised, too.[4] These treatments involve ingenious though approximate meldings of liquid structure theory with linear models of relaxation, often incorporating empirical information such as the frequency-dependent dielectric constant of the bulk solvent, $\epsilon(\omega)$.

We adopt a different approach, employing the perspective of a simple model of the solvent and the meaning of solvation. In particular, the solvent is described in terms of a linear responding field, i.e., a Gaussian field, that is expelled from the region of space occupied by the solute. Standard dielectric theory is an example of this class of models. The mean spherical approximation is another example as it corresponds to approximating a nonlinear system by a Gaussian model.[5] We show how the statistical mechanical analysis of solvation dynamics of this class of models can be carried out analytically, without approximation. The results derived from the analysis differ significantly from predictions often found in the literature.

Our most important findings concern the effects of solute size and shape on dielectric relaxation. The exclusion of solvent from the region occupied by the solute influences the normal modes of the system, generally causing a spectrum of relaxation times. This effect arises when the size of the solute introduces one or more length scales that differ from the correlation length of the solvent. The effect can be illustrated with the simplest of dielectric models—a uniform cubic lattice of polarizable cells.[6] Where standard approximations to dielectric continuum theory would predict a single longitudinal relaxation time, τ_L, the exact analysis of the model generally gives a range of times between between τ_L and Debye's relaxation time, τ_D. This fact is demonstrated in section V.

Before reaching that point, we begin in section II where we identify the correlation function that must be computed to treat solvation dynamics. The analysis of this correlation function for the case of a Gaussian field model is carried out in section III. Our main result, eq 3.11, is a time-dependent generalization of Chandler's treatment of equilibrium solvation.[5] The result expresses the space−time response function of the solution in terms of that of the pure solvent and the volume occupied by the solute. The general result of section III has applications that extend beyond the phenomenon of dielectric relaxation.[7] In the context of this paper, however, eq 3.11 represents a compact solution to the time-dependent dielectric boundary value problem of arbitrary geometry.

In section IV, we describe a coarse-grained Gaussian model of a dielectric material. With this model and eq 3.11, well-known dielectric continuum results are derived in section V. These results are extended and the effects of solute size and shape are demonstrated. The paper is concluded in section VI with a brief discussion.

II. Dielectric Solvation Dynamics

Consider a solute molecule embedded in the solvent where the solute has two electronic states, the ground state (g) and the excited state (e). Ignoring interstate coupling, the nuclear Hamiltonian of the system can be written as

$$H = H_g|g\rangle\langle g| + H_e|e\rangle\langle e| \qquad (2.1)$$

where $H_g = H_g^{(0)} + H_s + H_{gs}$ and $H_e = H_e^{(0)} + H_s + H_{es}$. $H_g^{(0)}$ and $H_e^{(0)}$ are the gas phase Hamiltonians of the solute molecule at the ground state and the excited state, H_s is the Hamiltonian of the solvent, and H_{gs} and H_{es} are the interactions between the solute and the solvent in the two electronic states.

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Imagine that the solvent was initially in equilibrium with the solute in its ground electronic state. After instantaneous excitation from the ground state to the excited state, the surrounding solvent molecules will relax to a new equilibrium consistent with the excited state. This relaxation is probed by ultrafast spectroscopy experiments[1] that measure

$$S(t) = \frac{\omega(t) - \omega(\infty)}{\omega(0) - \omega(\infty)} \tag{2.2}$$

where the time-dependent fluorescence frequency is given by

$$\hbar\omega(t) = \hbar\omega_0 + \Delta E(t) \tag{2.3}$$

Here, $\hbar\omega_0 = H_e^{(0)} - H_g^{(0)}$ is the gas phase frequency shift, and $\Delta E(t)$ is the solvation energy change due to the charge distribution change between the two electronic states. As such, the solvation correlation function can be rewritten in terms of the time variation of the solvation energy,

$$S(t) = \frac{\Delta E(t) - \Delta E(\infty)}{\Delta E(0) - \Delta E(\infty)} \tag{2.4}$$

To estimate the time-dependent solvation energy change, we will assume that the solvent−solute interactions, H_{gs} and H_{es}, differ only insofar as the charge distributions of the ground and excited states differ. In that case,

$$\Delta E(t) = \int d\mathbf{r}\, \mathbf{P}(\mathbf{r},t)\cdot\Delta E(\mathbf{r},t) \tag{2.5}$$

where $\Delta E(\mathbf{r},t) = \theta(t)\Delta E(\mathbf{r})$, with $\Delta E(\mathbf{r})$ denoting the change in electric field due to the instantaneous change in charge distribution of the solute at time zero, and $\mathbf{P}(\mathbf{r},t)$ is the subsequent induced polarization of the solvent. According to linear response theory[8]

$$\mathbf{P}(\mathbf{r},t) = \int_0^t dt' \int d\mathbf{r}\, \boldsymbol{\chi}^{(m)}(\mathbf{r},\mathbf{r}';t-t')\cdot\Delta E(\mathbf{r}',t') \tag{2.6}$$

where $\boldsymbol{\chi}^{(m)}(\mathbf{r},\mathbf{r}';t)$ is the susceptibility tensor of the solution. Thus, to the extent that the linear response description is valid, the solvation energy change can be expressed as

$$\Delta E(t) = \int_0^t dt' \int d\mathbf{r} \int d\mathbf{r}'\, \Delta E(\mathbf{r},t)\cdot\boldsymbol{\chi}^{(m)}(\mathbf{r},\mathbf{r}';t-t')\cdot\Delta E(\mathbf{r}',t') \tag{2.7a}$$

Its Laplace transform is

$$\Delta\tilde{E}(s) = \frac{1}{s}\int d\mathbf{r} \int d\mathbf{r}'\, \Delta E(\mathbf{r})\cdot\tilde{\boldsymbol{\chi}}^{(m)}(\mathbf{r},\mathbf{r}';s)\cdot\Delta E(\mathbf{r}') \tag{2.7b}$$

The dielectric susceptibility, $\tilde{\boldsymbol{\chi}}^{(m)}(\mathbf{r},\mathbf{r}';s)$, is the response function as *modified* by the presence of the solute (hence the superscript m). The modified response function generally differs from that of the pure solvent, $\tilde{\boldsymbol{\chi}}(\mathbf{r}-\mathbf{r}';s)$. A conventional way to estimate $\tilde{\boldsymbol{\chi}}^{(m)}(\mathbf{r},\mathbf{r}';s)$ in terms of $\tilde{\boldsymbol{\chi}}(\mathbf{r}-\mathbf{r}';s)$ is to assume that the solvent outside the volume occupied by the solute remains the same as the bulk solvent, namely behaves like an unperturbed pure isotropic solvent. The only effect of the solute is on the volume of the integration in eq 2.7. This assumption is the "uniform" or "homogeneous" dielectric approximation used in many of the solvation dynamics theories; see, for example, discussions of this and alternative approximations in refs 1 and 4. We will see that this approximation is generally not accurate because the excluded volume significantly affects dipole−dipole correlations outside the excluded volume. For the case of a linear responding dipole field, the change in correlations due

to the excluded volume can be computed exactly as we now demonstrate.

III. Gaussian Field Model of the Solution

Consider a time-dependent Gaussian model with action

$$S[\mathbf{m}(\mathbf{r},\tau)] = -\frac{1}{2}\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int_0^{\beta\hbar}\frac{d\tau'}{\beta\hbar}\int d\mathbf{r}\int d\mathbf{r}'\, \mathbf{m}(\mathbf{r},\tau)\cdot\mathbf{C}^{-1}(\mathbf{r},\mathbf{r}';\tau-\tau')\cdot\mathbf{m}(\mathbf{r}',\tau') \tag{3.1}$$

The tensor $\mathbf{C}^{-1}(\mathbf{r},\mathbf{r}';\tau-\tau')$ denotes the functional inverse of the autocorrelation function,

$$\mathbf{C}(\mathbf{r},\mathbf{r}';\tau-\tau') = \langle\mathbf{m}(\mathbf{r},\tau)\mathbf{m}(\mathbf{r}',\tau')\rangle \tag{3.2}$$

where $\mathbf{m}(\mathbf{r},\tau)$ is the dipole density at position $\mathbf{r}$ and Euclidean time τ. The pointed brackets denote the equilibrium thermal ensemble average, and β^{-1} stands for temperature in units of Boltzmann's constant. The action (3.1) involving only a dipole field is a reduced description of a solvent. One must imagine that other fields, such as density, have been integrated out. It is for this reason that the action must be nonlocal in time. A quadratic action is the simplest possibility. Nonlinear effects such as saturation are beyond the scope of the model. On a sufficiently coarse-grained level, resolving only those length scales larger than the correlation length of the fluid, the quadratic action can be viewed as exact. In the next section, the concept of a resolution length is made explicit, and is denoted there as the length a.

A solute excludes dipole density from the region occupied by the solute. The partition function for the solvent in the presence of the solute is

$$Z[E(\mathbf{r},\tau)] = \int D\mathbf{m}(\mathbf{r},\tau)\Big\{\prod_{\mathbf{r}\text{ inside}}\delta[\mathbf{m}(\mathbf{r},\tau)]\Big\}\exp\{S[\mathbf{m}(\mathbf{r},\tau),E(\mathbf{r},\tau)]\} \tag{3.3}$$

where the symbol D indicates that the integration is a functional integration, and the action is given by

$$S[\mathbf{m}(\mathbf{r},\tau),E(\mathbf{r},\tau)] = S[\mathbf{m}(\mathbf{r},\tau)] + \int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int d\mathbf{r}\, \mathbf{m}(\mathbf{r},\tau)\cdot E(\mathbf{r},\tau) \tag{3.4}$$

where $E(\mathbf{r},\tau)$ is the auxiliary field from which correlation functions can be generated by differentiation. It includes the electric field due to the solute on the solvent. The δ-functions in eq 3.3 account for the excluded volume effect due to the solute, where the terminology "$\mathbf{r}$ inside" indicates the space from which the solute excludes the solvent.

With the Fourier representation of the δ-functions, the partition function of the system can be rewritten as

$$Z[E(\mathbf{r},\tau)] = \int D\mathbf{m}(\mathbf{r},\tau)\int D\psi(\mathbf{r},\tau)\exp\{S[\mathbf{m}(\mathbf{r},\tau),E(\mathbf{r},\tau),\psi(\mathbf{r},\tau)]\} \tag{3.5}$$

with the action

$$S[\mathbf{m}(\mathbf{r},\tau),E(\mathbf{r},\tau),\psi(\mathbf{r},\tau)] = S[\mathbf{m}(\mathbf{r},\tau),E(\mathbf{r},\tau)] + i\int_{\text{in}}d\mathbf{r}\, \mathbf{m}(\mathbf{r},\tau)\cdot\psi(\mathbf{r},\tau) \tag{3.6}$$

where "in" indicates the the integration is over the "$\mathbf{r}$ inside" domain. Since the action is still of Gaussian form, the integrations can be performed in the standard way,[10] giving

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$$Z[\mathcal{E}(\mathbf{r},\tau)] \propto \exp\Big\{\frac{1}{2}\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int_0^{\beta\hbar}\frac{d\tau'}{\beta\hbar}\int d\mathbf{r}\int d\mathbf{r}' \times$$

$$\mathcal{E}(\mathbf{r},\tau)\cdot\mathbf{C}^{(m)}(\mathbf{r},\mathbf{r}';\tau-\tau')\cdot\mathcal{E}(\mathbf{r}',\tau')\Big\} \quad (3.7)$$

where

$$\mathbf{C}^{(m)}(\mathbf{r},\mathbf{r}';\tau-\tau') =$$

$$\mathbf{C}(\mathbf{r},\mathbf{r}';\tau-\tau') - \int_0^{\beta\hbar}\frac{d\tau''}{\beta\hbar}\int_0^{\beta\hbar}\frac{d\tau'''}{\beta\hbar}\int\int_{in}d\mathbf{r}''\,d\mathbf{r}''' \times$$

$$\mathbf{C}(\mathbf{r},\mathbf{r}'';\tau-\tau'')\cdot\mathbf{C}_{in}^{-1}(\mathbf{r}'',\mathbf{r}''';\tau''-\tau''')\cdot\mathbf{C}(\mathbf{r}''',\mathbf{r}';\tau'''-\tau') \quad (3.8)$$

The function $\mathbf{C}_{in}^{-1}(\mathbf{r},\mathbf{r}';\tau-\tau')$ denotes the inverse of

$$\mathbf{C}_{in}(\mathbf{r},\mathbf{r}';\tau-\tau') = \begin{cases} \mathbf{C}(\mathbf{r},\mathbf{r}';\tau-\tau'), & \mathbf{r}\text{ and }\mathbf{r}'\text{ inside} \\ 0, & \text{otherwise} \end{cases} \quad (3.9)$$

Using the partition function as a generating functional, we see that $\mathbf{C}^{(m)}(\mathbf{r},\mathbf{r}';\tau-\tau')$ given by eq 3.8 is the Euclidean time dipole−dipole correlation function.

The convolutions in time can be diagonalized by Fourier transform,

$$\hat{\mathbf{C}}^{(m)}(\mathbf{r},\mathbf{r}';\omega_n) = \hat{\mathbf{C}}(\mathbf{r},\mathbf{r}';\omega_n) -$$

$$\int\int_{in}d\mathbf{r}''\,d\mathbf{r}'''\,\hat{\mathbf{C}}(\mathbf{r},\mathbf{r}'';\omega_n)\cdot\hat{\mathbf{C}}_{in}^{-1}(\mathbf{r}'',\mathbf{r}''';\omega_n)\cdot\hat{\mathbf{C}}(\mathbf{r}''',\mathbf{r}';\omega_n)$$

$$(3.10)$$

where $\omega_n = 2\pi n/\beta\hbar$ is the usual Matsubara frequency. This function of discrete frequencies can be analytically continued to the entire complex plane of the frequency to give the Laplace transform of the real time susceptibility tensor, $\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s) = \beta\hat{\mathbf{C}}^{(m)}(\mathbf{r},\mathbf{r}';-is)$.[11] That is,

$$\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s) = \tilde{\chi}(\mathbf{r},\mathbf{r}';s) -$$

$$\int\int_{in}d\mathbf{r}''\,d\mathbf{r}'''\,\tilde{\chi}(\mathbf{r},\mathbf{r}'';s)\cdot\tilde{\chi}_{in}^{|Pv1}(\mathbf{r}'',\mathbf{r}''';s)\cdot\tilde{\chi}(\mathbf{r}''',\mathbf{r}';s) \quad (3.11)$$

Here, $\tilde{\chi}_{in}(\mathbf{r},\mathbf{r}')$ is the matrix with elements $\tilde{\chi}(\mathbf{r},\mathbf{r}')$ for both $\mathbf{r}$ and $\mathbf{r}'$ confined to the volume excluded by the solute. Its inverse has elements $\tilde{\chi}_{in}^{-1}(\mathbf{r},\mathbf{r}')$. Equation 3.11 is a time-dependent generalization of Chandler's eq 4.1 in ref 5. It is our fundamental result relating the susceptibility tensor of the solution to that of the pure solvent.

Equation 3.11 should be contrasted with the "uniform" dielectric approximation,[1]

$$\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s) \approx \tilde{\chi}_{out}(\mathbf{r},\mathbf{r}';s) \quad (3.12)$$

where

$$\tilde{\chi}_{out}(\mathbf{r},\mathbf{r}';s) = \begin{cases} \tilde{\chi}(\mathbf{r},\mathbf{r}';s), & \mathbf{r}\text{ and }\mathbf{r}'\text{ outside} \\ 0, & \text{otherwise} \end{cases} \quad (3.13)$$

This approximation should not be confused with dielectric continuum theory. Equation 3.12 neglects the influence of excluded volume on the polarization field outside that volume. The accuracy of this approximation to dielectric continuum theory can be judged from the results shown in section V.

If the dielectric response function is known for the pure solvent, the dielectric response function for the solution, which in general will not be uniform and isotropic, can be calculated from eq 3.11. This equation is the formal solution to the general time-dependent dielectric boundary value problem. It reduces the solutions to all such problems to the calculation of a matrix inverse, $\tilde{\chi}_{in}^{-1}(\mathbf{r},\mathbf{r}';s)$. An equivalent matrix formulation can be

derived with projection operators that focus on the "outside" region as opposed to the complement, "inside". The "outside" formulation can be most convenient for bounded systems. For the case of microscopic solutes in a macroscopic volume, "inside" is by far the smaller of the two volumes. For the solvation case, therefore, the "inside" formulation is the most convenient.

In either of its formulations, eq 3.11 is independent of the electric field $\mathcal{E}(\mathbf{r},\tau)$. This feature is a consequence of the Gaussian assumption. It means that the response function is independent of the charge distribution of the solute. The solvent response is, however, affected by the excluded volume of the solute as eq 3.11 demonstrates explicitly.

IV. Coarse-Grained Gaussian Model

To illustrate the use of these formulas, a theory for $\tilde{\chi}(\mathbf{r},\mathbf{r}';s)$ is required. For this purpose, we use the simplest textbook model of a dielectric material,[6] suitably generalized. In particular, we imagine that the space is divided into a cubic grid of N polarizable cells. Each cell has volume $v = a^3$, where a is the resolution length or correlation length of the material. The instantaneous dipole of the cell at discrete position $\mathbf{r}$ is $\mathbf{m}_\mathbf{r}(\tau) = \mathbf{m}(\mathbf{r},\tau)v$. The polarizability of each cell is nonlocal in time in this reduced description, and different cells interact via dipole−dipole interactions. Thus the action of the system can be written as

$$S[\mathbf{m}_\mathbf{r}(\tau)] = -\frac{\beta}{2}\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\int_0^{\beta\hbar}\frac{d\tau'}{\beta\hbar}\sum_\mathbf{r}\alpha^{-1}(\tau-\tau')\mathbf{m}_\mathbf{r}(\tau)\cdot\mathbf{m}_\mathbf{r}(\tau') -$$

$$\frac{\beta}{2}\int_0^{\beta\hbar}\frac{d\tau}{\beta\hbar}\sum_{\mathbf{r}\neq\mathbf{r}'}\mathbf{m}_\mathbf{r}(\tau)\cdot\nabla\nabla\frac{1}{|\mathbf{r}-\mathbf{r}'|}\cdot\mathbf{m}_\mathbf{r}(\tau) \quad (4.1)$$

With the Fourier series representations of

$$\mathbf{m}_\mathbf{r}(\tau) = \sum_\mathbf{k}\hat{\mathbf{m}}_\mathbf{k}(\tau)e^{i\mathbf{k}\cdot\mathbf{r}} \quad (4.2)$$

and

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{Nv}\sum_\mathbf{k}\frac{4\pi}{k^2}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \quad (4.3)$$

the action of the system can be written as

$$S = -\frac{N\beta}{2}\sum_\mathbf{k}\sum_n\hat{\mathbf{m}}_{\mathbf{k},n}\cdot\left[\frac{\mathbf{I}}{\alpha_n}+\frac{\hat{\mathbf{T}}(\mathbf{k})}{v}\right]\hat{\mathbf{m}}_{-\mathbf{k},-n} \quad (4.4)$$

Here $\hat{\mathbf{m}}_{\mathbf{k},n}$ is the Fourier component of $\hat{\mathbf{m}}_\mathbf{k}(\tau)$ at Matsubara frequency $\omega_n = 2n\pi/\beta\hbar$, and α_n is the Fourier component of $\alpha(\tau)$. Further,

$$\hat{\mathbf{T}}(\mathbf{k}) = \frac{4\pi}{3}\mathbf{I} - 4\pi\frac{\mathbf{kk}}{k^2} \quad (4.5)$$

where $\mathbf{I}$ is the rank-2 unit tensor. Due to the grid resolution, there is a finite range of wavevectors. From the completeness,

$$\delta_{\mathbf{r},\mathbf{r}'} = \frac{1}{N}\sum_\mathbf{k}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \quad (4.6)$$

the largest wavevector is estimated as $k_c \simeq (6\pi^2)^{1/3}/a$.

With the action (4.4), the correlation function tensor can be evaluated,

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$$\hat{\mathbf{C}}_{\mathbf{k},n} = \langle \hat{\mathbf{m}}_{\mathbf{k},n} \hat{\mathbf{m}}_{-\mathbf{k},-n} \rangle$$

$$= \frac{1}{N\beta}\left[\frac{\mathbf{I}}{\alpha_n} + \frac{\hat{\mathbf{T}}(\mathbf{k})}{v}\right]^{-1}$$

$$= \frac{1}{N\beta}\frac{\alpha_n}{(1-y_n)}\left[\mathbf{J}_-(\mathbf{k}) + \frac{1-y_n}{1+y_n}\mathbf{J}_+(\mathbf{k})\right] \quad (4.7)$$

where

$$y_n = \frac{4\pi}{3}\rho\alpha_n, \qquad \rho = \frac{1}{v} \quad (4.8)$$

and

$$\mathbf{J}_-(\mathbf{k}) = \mathbf{I} - \frac{\mathbf{kk}}{k^2}, \qquad \mathbf{J}_+(\mathbf{k}) = \frac{\mathbf{kk}}{k^2} \quad (4.9)$$

The third equality in eq 4.7 follows from the algebra of $\mathbf{J}_-$ and $\mathbf{J}_+$.[12]

By performing the inverse Fourier transform to real space, eq 4.7 gives

$$\hat{\mathbf{C}}(\mathbf{r}-\mathbf{r}';\omega_n) =$$
$$\frac{\alpha_n}{\beta(1-y_n)}\left[\frac{1+y_n}{1+2y_n}\delta_{\mathbf{r},\mathbf{r}'}\mathbf{I} + \frac{3y_n}{1+2y_n}\frac{v}{4\pi}\mathbf{T}(\mathbf{r}-\mathbf{r}')\right] \quad (4.10)$$

where

$$\mathbf{T}(\mathbf{r}) = 3\frac{\mathbf{rr}}{r^5} - \frac{\mathbf{I}}{r^3} \quad (4.11)$$

is the inverse Fourier transform of $\hat{\mathbf{T}}(\mathbf{k})$. The connections between $\hat{\mathbf{C}}(\mathbf{r}-\mathbf{r}';\omega_n)$ and the dielectric constant[12] provide a link between the cell polarizability and the dielectric constant. Specifically, at each Matsubara frequency, eq 4.7 implies $(\epsilon_n - 1)/(\epsilon_n + 2) = 4\pi\rho\alpha_n/3$. Analytical continuation of this equation gives the Clausius−Mossotti equation

$$\frac{\epsilon(s) - 1}{\epsilon(s) + 2} = \frac{4\pi}{3}\rho\alpha(s) \quad (4.12)$$

Combining eqs 4.7 and 4.10 therefore gives

$$\tilde{\chi}(\mathbf{r}-\mathbf{r}';s) = \frac{\epsilon(s)-1}{4\pi\rho}\left[\frac{(2\epsilon(s)+1)}{3\epsilon(s)}\delta_{\mathbf{r},\mathbf{r}'}\mathbf{I} + \frac{\epsilon(s)-1}{4\pi\rho\epsilon(s)}\mathbf{T}(\mathbf{r}-\mathbf{r}')\right] \quad (4.13)$$

The Debye model,

$$\epsilon(s) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1+s\tau_D} \quad (4.14)$$

expresses $\epsilon(s)$ in terms of the static dielectric constant, ϵ_0, a high-frequency dielectric constant, ϵ_∞, and Debye's relaxation time, τ_D. In the next section, we use the Debye model for illustrations because of its simplicity.

V. Solvation in the Coarse-Grained Model

In this section, the results of section IV are combined with eq 3.11. The spatial integration in eq 3.11 becomes summation over grid sites. According to the definition of solvation, the strategy of our calculation is to evacuate one or more cells to accommodate the solute. With the susceptibility given by eq 3.11, the solvation energy is evaluated from eq 2.7. We illustrate the approach with four examples.
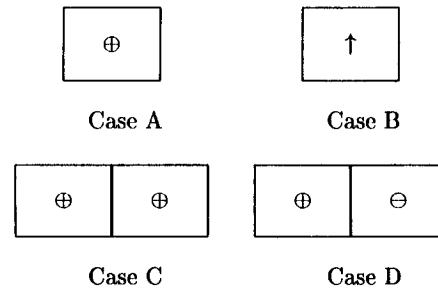
Figure 1. Geometries of four different solutes for which dielectric solvation dynamics is analyzed in the text.

A. Point Charge in a Single Cell. The simplest case is to evacuate the cell at the origin to introduce a unit point charge (Figure 1, Case A); the modified susceptibility will be

$$\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s) = \tilde{\chi}(\mathbf{r}-\mathbf{r}';s) - \tilde{\chi}(\mathbf{r}-\mathbf{0};s)\cdot\tilde{\chi}^{-1}(\mathbf{0}-\mathbf{0};s)\cdot\tilde{\chi}(\mathbf{0}-\mathbf{r}';s)$$
$$= \tilde{\chi}(\mathbf{r}-\mathbf{r}';s) - \{12\pi\rho\epsilon(s)/[\epsilon(s)-1][2\epsilon(s)+1]\}\tilde{\chi}(\mathbf{r};s)\cdot\tilde{\chi}(\mathbf{r}';s) \quad (5.1)$$

For a sudden change of unit charge at the origin, the electric field change at position $\mathbf{r}$ is

$$\Delta E = -\nabla\frac{1}{r} \quad (5.2)$$

Thus, combining eqs 5.1 and 5.2 with eq 2.7 gives

$$\Delta\tilde{E}(s) = \sum_{\mathbf{r}}\sum_{\mathbf{r}'}\nabla\frac{1}{r}\cdot\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s)\cdot\nabla\frac{1}{r'}$$
$$= \frac{1}{s}\left(\frac{48}{\pi}\right)^{1/3}\frac{1}{a}\left(1 - \frac{1}{\epsilon(s)}\right) \quad (5.3)$$

The second equality is most conveniently obtained from the first by introducing the Fourier representation of the summation and noting

$$\frac{1}{N}\sum_{\mathbf{k}}\frac{1}{k^2} = \frac{v}{2\pi^2}k_c \quad (5.4)$$

Equation 5.3 is the standard dielectric continuum result for charge solvation. It is the Born solvation formula. Combining eq 5.3 with the Debye model, eq 4.14, predicts single exponential relaxation with the relaxation time $\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D$. This prediction is a well-known dielectric continuum theory result (see, for example, ref 1b).

B. Point Dipole in a Single Cell. If the cell at the origin of the grid is evacuated and a point dipole of size $\mathbf{p}$ is introduced (Figure 1, Case B), the electric field change away from the origin is

$$\Delta E = \mathbf{T}(\mathbf{r})\cdot\mathbf{p} \quad (5.5)$$

The solvation energy change is then

$$\Delta\tilde{E}(s) = \frac{1}{s}\sum_{\mathbf{r}}\sum_{\mathbf{r}'}\mathbf{p}\cdot\mathbf{T}(\mathbf{r})\cdot\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s)\cdot\mathbf{T}(\mathbf{r}')\cdot\mathbf{p} \quad (5.6)$$

where $\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s)$ is given by eq 5.1. Again, Fourier analysis allows one to evaluate the summations. The result is

$$\Delta\tilde{E}(s) = \frac{1}{s}\frac{8\pi}{3v}p^2\frac{\epsilon(s)-1}{2\epsilon(s)+1} \quad (5.7)$$

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Once again, this is a dielectric continuum result, this time for the solvation of a point dipole.[1] This result is different from that of the "uniform" dielectric approximation, eq 3.12, but the difference is usually small. Combining eq 5.7 with the Debye model, eq 4.14, predicts single exponential relaxation with a relaxation time $\tau'_L = \tau_D(2\epsilon_\infty + 1)/(2\epsilon_0 + 1)$. Again, this prediction is a well-known result of dielectric continuum theory.[13] It can be contrasted with the incorrect prediction of eq 3.12. Namely, eq 3.12 combined with eq 5.6 yields single exponential relaxation with the relaxation time τ_L.

C. Two Identical Point Charges in Two Cells. Unlike the previous examples, when the solute cavity introduces a second length scale, results obtained involve more than one relaxation time. For example, suppose the solute occupies two cells, one at the origin and another at **a**. Then, from eq 3.11 the modified susceptibility can be evaluated with $\mathbf{r}''$, $\mathbf{r}''' = \mathbf{0}$, or **a**. Namely,

$$\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s) = \tilde{\chi}(\mathbf{r}-\mathbf{r}';s) - \tilde{\chi}^{(c)}(\mathbf{r},\mathbf{r}';s) \quad (5.8)$$

where

$$\tilde{\chi}^{(c)}(\mathbf{r},\mathbf{r}';s) = \frac{4\pi}{\epsilon(s)-1}(\tilde{\chi}(\mathbf{r}-0;s),\tilde{\chi}(\mathbf{r}-\mathbf{a};s))\cdot\begin{pmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{A}_2 & \mathbf{A}_1 \end{pmatrix}\cdot$$
$$(\tilde{\chi}(\mathbf{r}'-0;s),\tilde{\chi}(\mathbf{r}'-\mathbf{a};s)) \quad (5.9)$$

$\tilde{\chi}(\mathbf{r}-\mathbf{r}';s)$ is given by eq 4.13, which gives the uniform contribution to the solvation energy (this part gives the "uniform" dielectric approximation). $\tilde{\chi}^{(c)}(\mathbf{r},\mathbf{r}',s)$ describes the nonuniform contribution to the solvation energy due to the cell evacuation. The matrices $\mathbf{A}_1$ and $\mathbf{A}_2$ are given by

$$\mathbf{A}_1 = \frac{c_1}{c_1^2 - c_2^2}\mathbf{J}_-(\mathbf{a}) + \frac{c_1}{c_1^2 - 4c_2^2}\mathbf{J}_+(\mathbf{a})$$

$$\mathbf{A}_2 = \frac{c_2}{c_1^2 - c_2^2}\mathbf{J}_-(\mathbf{a}) - \frac{2c_2}{c_1^2 - 4c_2^2}\mathbf{J}_+(\mathbf{a}) \quad (5.10)$$

with

$$c_1 = \frac{2\epsilon(s) + 1}{3\epsilon(s)}$$

and

$$c_2 = \frac{\epsilon(s) - 1}{4\pi\epsilon(s)}$$

If a unit charge is introduced in each of the evacuated sites at **0** and **a** (Figure 1c), the electric field change outside the cavity is

$$\Delta E = -\nabla\frac{1}{|\mathbf{r}|} - \nabla\frac{1}{|\mathbf{r} - \mathbf{a}|} \quad (5.11)$$

Therefore, the solvation energy is

$$\Delta\tilde{E}(s) =$$
$$\frac{1}{s}\sum_{\mathbf{r}}\sum_{\mathbf{r}'}\nabla\left(\frac{1}{|\mathbf{r}|} + \frac{1}{|\mathbf{r} - \mathbf{a}|}\right)\cdot\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s)\cdot\nabla\left(\frac{1}{|\mathbf{r}'|} + \frac{1}{|\mathbf{r}' - \mathbf{a}|}\right) \quad (5.12)$$

with $\tilde{\chi}^{(m)}(\mathbf{r},\mathbf{r}';s)$ given in eq 5.8. Evaluation of the summations are facilitated with the following relations,

$$\frac{1}{N}\sum_{\mathbf{k}}\frac{e^{i\mathbf{k}\cdot\mathbf{a}}}{k^2} = \frac{v}{2\pi^2}\frac{Si(k_c a)}{a} \quad (5.13)$$

$$\frac{1}{Nv}\sum_{\mathbf{k}}\frac{\mathbf{k}}{k^2}e^{i\mathbf{k}\cdot\mathbf{a}} = \frac{i\mathbf{a}}{2\pi^2 a^3}f_2 \quad (5.14)$$

where

$$f_2 = Si(k_c a) - \sin(k_c a) \quad (5.15)$$

and $Si(x)$ is the standard sine integral. **a** is taken to be $(0,0,a)$.

The evaluation gives

$$\Delta\tilde{E}(s) = \Delta\tilde{E}^{(0)}(s) - \Delta\tilde{E}^{(c)}(s) \quad (5.16)$$

where

$$\Delta\tilde{E}^{(0)}(s) = \frac{1}{s}\left(\frac{48}{\pi}\right)^{1/3}\frac{2}{a}\left(1 + \frac{Si(k_c a)}{k_c a}\right)\left(1 - \frac{1}{\epsilon(s)}\right) \quad (5.17)$$

and

$$\Delta\tilde{E}^{(c)}(s) = (12f_2^2/\pi^2 a)\frac{1}{s}\left(1 - \frac{1}{\epsilon(s)}\right)/\{2\pi[2\epsilon(s) + 1] - 3[\epsilon(s) - 1]\} \quad (5.18)$$

If eq 3.12 was used, the solvation energy predicted would be

$$\Delta\tilde{E}(s) \approx \Delta\tilde{E}^{(0)}(s) \quad (5.19)$$

Employing the Debye model, eq 4.14, one finds that eq 5.19 gives a single exponential relaxation with relaxation time τ_L. However, the full $\Delta E(t)$ from eq 3.11 and therefore eq 5.16 gives two relaxation times: τ_L and $[(4\pi - 3)\epsilon_\infty + (2\pi + 3)]\tau_D/[(4\pi - 3)\epsilon_0 + (2\pi + 3)]$. See Figure 2. Single exponential relaxation with time τ_L is often cited as the general prediction of dielectric continuum theory (see, for example, ref 1). We see, however, that it is the result of the "uniform" dielectric approximation, eq 3.12.

D. Two Opposite Sign Charges in Two Cells. For this case, with two evacuated cells filled with charges of opposite sign (Figure 1, Case D), the electric field change away from the cavity is

$$\Delta E = -\nabla\frac{1}{|\mathbf{r}|} + \nabla\frac{1}{|\mathbf{r} - \mathbf{a}|} \quad (5.20)$$
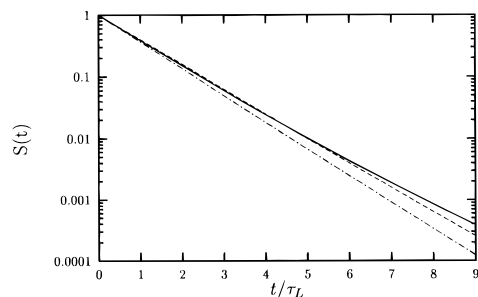
The calculation of the solvation energy proceeds as above. The result is

$$\Delta E^{(0)}(s) = \frac{1}{s}\left(\frac{48}{\pi}\right)^{1/3}\frac{2}{a}\left(1 - \frac{Si(k_c a)}{k_c a}\right)\left(1 - \frac{1}{\epsilon(s)}\right) \quad (5.21)$$

and

$$\Delta\tilde{E}^{(c)}(s) = (12f_2^2/\pi^2 a)\frac{1}{s}\left(1 - \frac{1}{\epsilon(s)}\right)/\{2\pi[2\epsilon(s) + 1] + 3[\epsilon(s) - 1]\} \quad (5.22)$$

Again, with the Debye model, eq 4.14, the full $\Delta E(t)$ from eqs 5.22 and 5.23 gives two relaxation times. In this case, the two times are τ_L and $[(4\pi + 3)\epsilon_\infty + (2\pi - 3)]\tau_D/[(4\pi + 3)\epsilon_0 + (2\pi - 3)]$. For typical values of ϵ_∞ and ϵ_0, these two times are close in value. See Figure 2.

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Figure 2. Solvation correlation function as a function of t/τ_L with ϵ_∞ = 2.0 and ϵ_0 = 40.0. The solid line is for the solute considered in Case C. The dashed line is for the solute considered in Case D. The dot−dash line corresponds to $S(t) = \exp(-t/\tau_L)$. This single exponential decay is the correct $S(t)$ for Case A and is the prediction of "uniform" dielectric approximation for Cases B, C, and D.

The predicted relaxation time longer than τ_L is in agreement with the experimental results.[14]

VI. Conclusions

The results of the previous section show that the simplest of models for a dielectric material, a uniform grid of polarizable cells, predicts that solvation dynamics is generally characterized by a spectrum of relaxation times. Even with the Debye model and dielectric continuum theory, single exponential relaxation is found only when the solute introduces no microscopic length scale of its own.

Polarization at the solute−solvent interface has a net average orientation. The effects of this orientation are propagated over relatively long distances through dipole−dipole interactions. The result of these effects is to couple the different components of the polarization field, components of different symmetries, and wavevectors. In the absence of the solute, the normal modes of the Gaussian model are the Fourier components of the polarization field. In the presence of the solute, the field is expelled from the region occupied by the solute, and the normal modes of the solvent are necessarily different.

This physics is efficiently and exactly described by eq 3.11. It is the generally applicable description of dipolar correlations induced by solutes of nontrivial size and shape. Indeed, eq 3.11 provides a compact matrix representation of the solutions to dielectric boundary value problems. The application of this equation is particularly simple when a coarse-grained description of the solvent is employed, as we have illustrated. For some molecular geometries, such as ellipsoids, the implementation of a continuum treatment can be straightforward, too.[15]

There remain, however, physically pertinent issues in solvation dynamics that are beyond the scope of eq 3.11. The equation rests on the assumption of a Gaussian polarization field and the neglect of density fluctuations. Extensions to describe nonlinear polarization response and also density fluctuations could use the exact treatment of the Gaussian model as the reference system in a perturbation theory. An issue that is often ignored in discussions of solvation dynamics[1] is the possibility that changes in state of the solute may also involve changes in the size and shape of the solute. Equation 3.11 does not address this issue. To extend the theory in this direction, one must imagine that the "in" and "out" manifolds can be time dependent.

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