Journal of Statistical Physics, Vol. 78, Nos. 1/2, 1995

Surrogate Hamiltonian Description of Solvation Dynamics. Site Number Density and Polarization Charge Density Formulations

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Received November 5, 1993

We explore a recently developed theory of solvation dynamics that analyzes the molecular response of the solvent to a sudden change of the charge distribution of a solute particle immersed in it. We derive an approximate nonequilibrium distribution function $f^h_\Sigma(\Gamma, t)$ for a "surrogate" Hamiltonian description of the solvation dynamics process. The surrogate Hamiltonian is expressed in terms of renormalized solute–solvent interactions, a feature that allows us to introduce a simple reduction scheme in the many-body dynamics problem without losing essential solute–solvent static correlations that rule the equilibrium solvation. With $f^h_\Sigma(\Gamma, t)$ in hand we calculate the solvation time correlation function in two ways. The first one, previously reported, is basically a "dielectric formulation" in which the local polarization charge density of the solvent is the primary dynamical variable that couples to the field of the solute. In the new development reported here, the "site number density formulation," the primary dynamical variables comprise the set of local solvent site number densities. We find that the dielectric formulation is embedded in the solvent site number density formulation as shown, for example, by comparing the respective time correlation functions of the solvation dynamics. An important feature of our approach is that at every stage the coupling between the solute and solvent is formulated in terms of the solute–solvent intermolecular interactions, rather than some sort of cavity construction. Furthermore, both the solute and the solvent molecules are represented by interaction site models. Applications of the dielectric theory are illustrated with calculations of the solvation dynamics of a cation in water and an exploration of the effect of the details of the charge distribution on the solvation dynamics of a benzenelike solute in acetonitrile.

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0022-4715/95/0100-0239$07.50/0 © 1995 Plenum Publishing Corporation

KEY WORDS: Solvation dynamics; solvation time correlation function; dielectric response; interaction site models; site number densities; polarization charge density.

1. INTRODUCTION

The influence of solvent dynamics upon chemical kinetic processes in liquids has attracted much attention in recent years.$^{(1-4)}$ Considerable effort has been directed to the molecular interpretation of the solvation time correlation function (tcf)

$$\mathscr{X}(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \tag{1.1}$$

which is measured in time-resolved fluorescence Stokes shift experiments.$^{(1-3,5,6)}$ Here $\nu(t)$ is the fluorescence frequency at time t of a solute molecule that was suddenly excited at $t = 0$. The frequency $\nu(t)$ changes as the solvent adjusts to the excited-state charge distribution of the solute. Thus $\nu(t)$ and $\mathscr{X}(t)$ provide a way to monitor the global dynamic solvation response that follows the photoexcitation of the solute molecule.

Stimulated by the ever-increasing resolution of the experimental results$^{(1,2,5,6)}$ and also by theoretical predictions,$^{(3,7-19)}$ several laboratories have studied the solvation dynamics of various model solutes in realistic model solvents by molecular dynamics (MD) simulations.$^{(6,20-32)}$ Both the solvation tcf $\mathscr{X}(t)$ and its linear-response estimates $\mathscr{X}^{\mathrm{P}}(t)$ [the solute is in the ground or "precursor" (P) state] and $\mathscr{X}^{\mathrm{S}}(t)$ [the solute is in the excited or "successor" (S) state] have been computed by non-equilibrium and equilibrium MD simulations. These simulations revealed severe limitations in the earlier theories, in the majority of which the underlying solvent dynamics was represented in the Markovian limit and the solvent was modeled either as a dielectric continuum$^{(7,8,12)}$ or as a molecular fluid comprising hard spheres with embedded point dipoles$^{(3,9-11,13)}$ or several point multipoles.$^{(14)}$ In ref. 15 we presented a quasianalytical theory of solvation dynamics in which, for the first time, the solvent was represented by an interaction site model (ISM).[3] The dynamics, however, was represented as diffusive. More recently, improved quasianalytical model theories$^{(18,19)}$ and some correlations$^{(16,17)}$ have been reported, which are not limited to diffusive dynamics. These new developments have met considerable success in describing (even quantitatively) the features of $\mathscr{X}(t)$ for

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[3] In these models the potential energy of interaction between two molecules is a sum of site–site terms, including Coulombic interactions between partial charges q_j located at the molecular sites.

some model systems, but they are somewhat limited by the simple model representation of the solvent and the solute, and also by their reliance on cavity constructions to deal with the solute–solvent interactions.

In recent work(33, 34) we presented a new quasianalytical theory of solvation dynamics, under classical statistical mechanics, with several distinctive features. (a) The theory is based on a new *renormalized* linear response development, based on a *surrogate* Hamiltonian which incorporates nonlinear aspects of the solute–solvent interactions in equilibrium solvation. (b) The solute–solvent coupling is expressed in terms of intermolecular interactions; no cavity constructions are needed. (c) Both the solute and the solvent are represented by rigid nonpolarizable interaction site models, of the same type as those employed in most simulations. (d) The dynamical aspects of the theory are treated with the reference memory function approximation(15, 35–37) (RMFA), which goes beyond the Markovian approximation. These features considerably extend the scope of our initial work(15) in the theory of solvation dynamics.

The surrogate Hamiltonian in item (a) can be contrasted with the *factual* Hamiltonian, written in terms of bare or unshielded solute–solvent interactions. The new theory(33, 34) is based on the premise that accurate results for the solvent response may be derived from an approximate treatment of the dynamical problem cast in terms of a surrogate time-dependent Hamiltonian obtained by renormalizing the bare interactions in an appropriate way.

In the earlier work(33, 34) the renormalization of the solute–solvent interactions has a distinct dielectric flavor; it is constructed with the solvent polarization charge density as the dynamical variable that couples the solvent to the renormalized field of the solute. We refer to this as the *dielectric formulation* of the surrogate theory. Here we explore the surrogate Hamiltonian theory of solvation dynamics by turning to an alternative renormalization of the solute–solvent interactions in which the solvent site number densities are the primary dynamical variables. We find that the solvent response includes not only the dielectric part considered before,(33, 34) but also another dynamical part that (at equal times) is orthogonal to the dielectric part. It is shown that the dielectric formulation of refs. 33 and 34 is recovered from the solvent site number density formulation if we neglect the orthogonal part.

We begin in Section 2 with a brief description of the dynamic solvation experiment, with the purpose of introducing certain concepts and notation. In Section 3 we apply the general formulation of nonequilibrium statistical mechanics to derive an approximation $f^h_\Sigma(\Gamma, t)$ for the nonequilibrium distribution function of the solvent in the field of the solute. Although the formulation is very similar to Kubo's theory of linear response to mechanical perturbations,(38) the development does not assume linear response in the conventional way. Instead, linear response to a surrogate perturbation (which may be nonlinear with respect to the bare perturbation) arises as the direct consequence of a linearization with respect to renormalized interactions $\hat{\Psi}^D_\Sigma$ between the solute and the solvent. An important feature of the development is its generality; the renormalized solute–solvent interactions $\hat{\Psi}^D_\Sigma$ that define $f^h_\Sigma(\Gamma, t)$ still need to be specified. At the same level of generality, we examine in Section 4 the form of the expectation values of dynamical variables calculated under $f^h_\Sigma(\Gamma, t)$. The analysis suggests a simple and natural scheme for specifying the renormalized solute–solvent interactions $\hat{\Psi}^D_\Sigma$. We also show in this section that under $f^h_\Sigma(\Gamma, t)$, the solvation tcf can be expressed in terms of a normalized equilibrium tcf governed by the Hamiltonian of the homogeneous solvent, while the influence of the solute is incorporated in the dynamical variables. Based on the results of Section 4, in Section 5 we develop the site number density formulation of the renormalized solute–solvent coupling $\hat{\Psi}^D_\Sigma$. In Section 6 we show how the previously reported(33, 34) dielectric formulation is embedded in the site number density formulation of Section 5. Some model calculations under the dielectric formulation are reported in Section 6. In Section 7 we summarize our main results.

2. THE DYNAMIC SOLVATION EXPERIMENT

We consider one ISM solute molecule in an ISM solvent. The solute can be in either of two electronic states: the precursor (P) state, with site partial charges $\{Q^{\mathrm{P}}_\lambda\}$, or the successor (S) state, with site partial charges $\{Q^{\mathrm{S}}_\lambda\}$.[4] We assume that the solute in the excited state returns to the electronic ground state by fluorescence on a time scale that is comparable with the structural relaxation rate of the solvent around the solute. We regard the solute as the source of an "external" field which is *fixed* in space, and we follow the solvent dynamics driven by this field.[5] Throughout this paper the subscript λ refers to the interaction sites of the solute, while the subscript aj refers to interaction site j of solvent molecule a.

At times $t<0$ the solvent is in equilibrium with the solute in the P state; the average solvent structure around the solute is characterized by the solute–solvent set of site–site pair correlation functions $h^{\mathrm{P}}_{\lambda j}(r)$. At $t=0$ a photon of energy $h\nu_{\mathrm{abs}}$ excites the solute to the S state. At $t=0^+$ the

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[4] The superscript D is used to denote either P or S.

[5] Only those microscopic properties that depend on the coordinates and momenta of the solvent sites are dynamical variables. In this work collective dynamical variables are distinguished with a caret.

structure of the solvent around the solute is still described by the set $h^{\mathrm{P}}_{\lambda j}(r)$, as follows from the Franck–Condon principle. Then the frequency $\nu(t)$ of the time-dependent fluorescence evolves from $\nu(0^+) = \nu_{\mathrm{abs}}$ as the solvent adapts to the new charge distribution $\{Q^{\mathrm{S}}_\lambda\}$ of the solute. The relaxation continues until the solvent is in equilibrium with the solute in the S state; then the average structure is described by the successor set of solute–solvent site–site pair correlation functions $h^{\mathrm{S}}_{\lambda j}(r)$. In this limit the frequency of the fluorescence $\nu(\infty) = \nu_{\mathrm{flr}}$ becomes independent of time.

The fluorescence frequency at time t is given by[12, 27]

$$h\nu(t) = h\nu_0 + \langle \hat{\mathscr{U}}; t\rangle \tag{2.1}$$

where ν_0 is the emission frequency of the S → P transition of the solute molecule in vacuum, while

$$\langle \hat{\mathscr{U}}; t\rangle = \int d\Omega\; p(\Omega) \int d\Gamma\, f(\Gamma, t)\hat{\mathscr{U}} \tag{2.2}$$

is the expectation value of the *bare* electrostatic energy gap

$$\hat{\mathscr{U}} = \sum_{\lambda} \sum_{aj} \frac{\Delta Q_\lambda q_j}{r_{\lambda, aj}} \tag{2.3}$$

under $f(\Gamma, t)$, the nonequilibrium distribution function that describes the state Γ of the solvent under the field of the solute at time t.[6] In Eq. (2.3) we define $\Delta Q_\lambda \equiv Q^{\mathrm{S}}_\lambda - Q^{\mathrm{P}}_\lambda$ as the change of the partial charge of solute site λ in the P → S transition. Furthermore, $r_{\lambda,aj} = |\mathbf{r}_{\lambda,aj}|$ (with $\mathbf{r}_{\lambda,aj} \equiv \mathbf{r}_{aj} - \mathbf{r}_\lambda$) is the distance between site j of solvent molecule a and solute site λ, and q_j is the partial charge of the type j solvent site.

From Eqs. (1.1) and (2.1) we have

$$\mathscr{S}(t) = \frac{\langle \hat{\mathscr{U}}; t\rangle - \langle \hat{\mathscr{U}}; \infty\rangle}{\langle \hat{\mathscr{U}}; 0\rangle - \langle \hat{\mathscr{U}}; \infty\rangle} \tag{2.4}$$

where $\langle \hat{\mathscr{U}}; 0\rangle$ and $\langle \hat{\mathscr{U}}; \infty\rangle$ are the respective values of $\langle \hat{\mathscr{U}}; t\rangle$ at $t = 0^+$ (just after the photoexcitation) and $t \to \infty$ (when the solvent has equilibrated to the S charge distribution of the solute).

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[6] More precisely, $f(\Gamma, t)$ is the conditional probability density that at time t the coordinates and momenta of the solvent sites are $\Gamma = \{\mathbf{r}_{aj}, \mathbf{p}_{aj}\}$ given that at time $t = 0$ the solute had orientation Ω. Correspondingly, $p(\Omega)$ is the probability density for the solute to have orientation Ω at $t = 0$.

The solvent distribution function satisfies $f(\Gamma, 0) = f^{\mathrm{P}}_{\mathrm{eq}}(\Gamma) \sim \exp(-\beta H^{\mathrm{P}})$ at $t = 0$ and $f(\Gamma, \infty) = f^{\mathrm{S}}_{\mathrm{eq}}(\Gamma) \sim \exp(-\beta H^{\mathrm{S}})$ at $t = \infty$, where $\beta = (k_{\mathrm{B}} T)^{-1}$ is the inverse of the temperature in energy units, and H^D is the *factual* Hamiltonian of the solvent in the field of the solute at state D

$$H^D = H_{\mathrm{w}} + \hat{\Psi}^* + \hat{\Psi}^{l,D}, \qquad D = \mathrm{P, S} \tag{2.5}$$

Here H_{w} is the Hamiltonian of the pure solvent, while $\hat{\Psi}^*$ and $\hat{\Psi}^{l,D}$ are, respectively, the short-range and the long-range (Coulombic) parts of the solute–solvent potential energy of interaction. We assume that the short-range interactions $\hat{\Psi}^*$ are independent of the solute state. On the other hand,

$$\hat{\Psi}^{l,D} = \sum_{\lambda} \sum_{aj} \frac{Q^D_{\lambda} q_j}{r_{\lambda,aj}} \tag{2.6}$$

depends on the solute state through the solute partial charges Q^D_{λ}. From Eqs. (2.3), (2.5), and (2.6) it follows that[33, 34]

$$\hat{\mathscr{U}} = H^{\mathrm{S}} - H^{\mathrm{P}} = \hat{\Psi}^{l,\mathrm{S}} - \hat{\Psi}^{l,\mathrm{P}} \tag{2.7}$$

The development in Eqs. (2.1)–(2.7) comprises the *factual* description of the solvation dynamics experiment; it is faithful to the original Hamiltonian model of the solute–solvent interactions, Eq. (2.5).

To calculate the solvation tcf $\mathscr{S}(t)$ from Eq. (2.4) we need to know $\langle \hat{\mathscr{U}}; t \rangle$ in the range between $t = 0^+$ and $t = \infty$. In computer simulation studies of solvation dynamics, nonlinear response of the solvent has been observed in certain cases, as revealed by the lack of agreement among: (i) $\mathscr{S}(t)$ calculated with Eq. (2.4) by nonequilibrium MD, (ii) the linear response estimate $\mathscr{S}^{\mathrm{P}}(t)$ based on time-dependent solvent fluctuations in equilibrium with the initial state of the solute, and (iii) the linear response estimate $\mathscr{S}^{\mathrm{S}}(t)$ based on time-dependent solvent fluctuations in equilibrium with the final state of the solute. The differences among the three tcf's provide a measure of the deviations from linear response. Particularly strong nonlinear effects have been reported by Fonseca and Ladanyi[26] in the solvation dynamics of dipolar solutes in methanol. The theory presented in the next section, although inherently a linear response theory, fares surprisingly well when its prediction for the solvation tcf is compared with $\mathscr{S}(t)$ calculated by nonequilibrium MD trajectories.[33, 34] On the other hand, another consequence of nonlinear response in solvation dynamics, namely the dependence with time of the lineshape of the fluorescence spectra of the solute, discussed in detail by Carter and Hynes,[27] is not captured by the theory presented in this work.

3. SURROGATE NONEQUILIBRIUM DISTRIBUTION FUNCTION OF THE SOLVENT

As in previous reports,(33, 34) we study a "surrogate" description of the solvation dynamics experiment in which the solute–solvent coupling is renormalized in a way that is consistent with a Hamiltonian formulation.

Like the factual description of Section 2, the surrogate description(33, 34) of the solvation dynamics experiment has the solute–solvent potential energy of interaction abruptly changing at $t=0$ from its form $\hat{\Psi}^{\mathrm{P}}_{\Sigma}$ when the solute is in the P state to the form $\hat{\Psi}^{\mathrm{S}}_{\Sigma}$ when the solute is in the S state. At $t<0$ and $t=\infty$ the solvent is in equilibrium with the solute in states P and S, respectively, and therefore is described by equilibrium distribution functions defined in terms of the surrogate Hamiltonians H^{P}_{Σ} and H^{S}_{Σ},

$$H^{D}_{\Sigma}=H_{w}+\hat{\Psi}^{D}_{\Sigma}, \qquad D=\mathrm{P},\mathrm{S} \tag{3.1}$$

In contrast with the factual description, however, $\hat{\Psi}^{\mathrm{P}}_{\Sigma}$ and $\hat{\Psi}^{\mathrm{S}}_{\Sigma}$ represent *renormalized* solute–solvent potential energies of interaction which in general may be nonlinear with respect to the bare interactions that appear in Eq. (2.5). Therefore, to avoid inconsistencies (i.e., not to overcount the interactions), the equations of the surrogate description are systematically linearized with respect to the renormalized interactions $\hat{\Psi}^{D}_{\Sigma}$. For example, the situations at $t<0$ and $t=\infty$ are described by the surrogate equilibrium distribution functions(33, 34)

$$f^{D}_{\Sigma,\mathrm{eq}}(\Gamma)\equiv f^{w}_{\mathrm{eq}}(\Gamma)[1-\beta\delta(\hat{\Psi}^{D}_{\Sigma})], \qquad D=\mathrm{P},\mathrm{S} \tag{3.2}$$

which result from the linearization of the equilibrium canonical distribution function $\sim\exp(-\beta H^{D}_{\Sigma})$ with respect to the renormalized solute–solvent interactions $\hat{\Psi}^{D}_{\Sigma}$. In Eq. (3.2) $f^{w}_{\mathrm{eq}}(\Gamma)$ is the equilibrium distribution function of the homogeneous solvent, i.e., $f^{w}_{\mathrm{eq}}(\Gamma)\sim\exp(-\beta H_{w})$. In reference to $\delta(\hat{\Psi}^{D}_{\Sigma})$ in Eq. (3.2), we note that in this paper we use the notations $\langle\hat{a}\rangle$ and $\delta\hat{a}$ to respectively indicate the average of a dynamical variable $\hat{a}$ under $f^{w}_{\mathrm{eq}}(\Gamma)$

$$\langle\hat{a}\rangle\equiv\int d\Omega\; p(\Omega)\int d\Gamma\, f^{w}_{\mathrm{eq}}(\Gamma)\hat{a} \tag{3.3a}$$

and the fluctuating part

$$\delta\hat{a}\equiv\hat{a}-\langle\hat{a}\rangle \tag{3.3b}$$

of $\hat{a}$ relative to its average value in the homogeneous solvent. Thus in Eq. (3.2) we have $\delta(\hat{\Psi}^{D}_{\Sigma})=\hat{\Psi}^{D}_{\Sigma}-\langle\hat{\Psi}^{D}_{\Sigma}\rangle$.

In the surrogate description, the solvation dynamics following the photoexcitation is governed by the Liouville operator $\mathscr{L}^{\mathrm{S}}_{\Sigma}$ associated with the surrogate Hamiltonian H^{S}_{Σ} of the solvent under the renormalized field of the solute in the S state. Thus, the surrogate counterpart $f_{\Sigma}(\Gamma, t)$ of the factual solvent distribution function $f(\Gamma, t)$ [cf. Eq. (2.2)] is the solution of Liouville equation

$$(\partial_t + \mathscr{L}^{\mathrm{S}}_{\Sigma})\, f_{\Sigma}(\Gamma, t) = 0 \tag{3.4a}$$

with the initial condition

$$f_{\Sigma}(\Gamma, 0) = f^{\mathrm{P}}_{\Sigma,\mathrm{eq}}(\Gamma) \tag{3.4b}$$

in which $f^{\mathrm{P}}_{\Sigma,\mathrm{eq}}(\Gamma)$ is given by Eq. (3.2) with $D = \mathrm{P}$.

It is convenient to separate the distribution function $f_{\Sigma}(\Gamma, t)$ and the Liouville operator $\mathscr{L}^{\mathrm{S}}_{\Sigma}$ each into two parts, one (index w) that is independent of the renormalized solute–solvent interactions $\hat{\Psi}^{D}_{\Sigma}$ and the other (index Ψ) that is *linear* in $\hat{\Psi}^{D}_{\Sigma}$:

$$f_{\Sigma}(\Gamma, t) = f^{w}_{\Sigma}(\Gamma, t) + f^{\Psi}_{\Sigma}(\Gamma, t) \tag{3.5a}$$

$$\mathscr{L}^{\mathrm{S}}_{\Sigma} = \mathscr{L}_{w} + \mathscr{L}^{\mathrm{S}}_{\Sigma,\Psi} \tag{3.5b}$$

where $\mathscr{L}_{w}$ is the Liouville operator of the homogeneous solvent. Then, according to the order in the solute–solvent interactions, Eq. (3.4a) separates into the equations

$$(\partial_t + \mathscr{L}_{w})\, f^{w}_{\Sigma}(\Gamma, t) = 0 \tag{3.6a}$$

$$(\partial_t + \mathscr{L}_{w})\, f^{\Psi}_{\Sigma}(\Gamma, t) = -\mathscr{L}^{\mathrm{S}}_{\Sigma,\Psi} f^{w}_{\Sigma}(\Gamma, t) \tag{3.6b}$$

which have the formal solution

$$f^{w}_{\Sigma}(\Gamma, t) = \mathscr{T}_{w}(t)\, f^{w}_{\Sigma}(\Gamma, 0) \tag{3.7a}$$

$$f^{\Psi}_{\Sigma}(\Gamma, t) = \mathscr{T}_{w}(t)\, y(t) = \mathscr{T}_{w}(t)\, y(0) - \int_0^t dt'\, \mathscr{T}_{w}(t - t')\, \mathscr{L}^{\mathrm{S}}_{\Sigma,\Psi} f^{w}_{\Sigma}(\Gamma, t') \tag{3.7b}$$

The first equality of Eq. (3.7b) defines the auxiliary function $y(t)$, while

$$\mathscr{T}_{w}(t) = \exp(-t\mathscr{L}_{w}) \tag{3.8}$$

is the propagator of the homogeneous solvent.

The calculation is completed with the initial condition, Eq. (3.4b), which separates according to the order in the renormalized interactions as

$$f_{\Sigma}^{w}(\Gamma, 0) = f_{\mathrm{eq}}^{w}(\Gamma) \tag{3.9a}$$

$$f_{\Sigma}^{\Psi}(\Gamma, 0) = -\beta f_{\mathrm{eq}}^{w}(\Gamma)\, \delta(\hat{\Psi}_{\Sigma}^{\mathrm{P}}) \tag{3.9b}$$

When Eq. (3.9a) is replaced in Eq. (3.7a) we have

$$f_{\Sigma}^{w}(\Gamma, t) = \mathscr{T}_{w}(t)\, f_{\mathrm{eq}}^{w}(\Gamma) = f_{\mathrm{eq}}^{w}(\Gamma) \tag{3.10a}$$

where in deriving the second equality we have taken into account that $\mathscr{L}_{w} f_{\mathrm{eq}}^{w}(\Gamma) = 0$. Using this result, we can replace $\mathscr{L}_{\Sigma,\Psi}^{\mathrm{S}} f_{\Sigma}^{w}(\Gamma, t')$ in the inhomogeneous term of Eq. (3.7b) by $\mathscr{L}_{\Sigma,\Psi}^{\mathrm{S}} f_{\mathrm{eq}}^{w}(\Gamma)$, for which we can apply the relation

$$\mathscr{L}_{\Sigma,\Psi}^{\mathrm{S}} f_{\mathrm{eq}}^{w}(\Gamma) = \beta f_{\mathrm{eq}}^{w}(\Gamma)(\mathscr{L}_{w} \hat{\Psi}_{\Sigma}^{\mathrm{S}})$$

Then Eqs. (3.7b) and (3.9b) give

$$f_{\Sigma}^{\Psi}(\Gamma, t) = -\beta f_{\mathrm{eq}}^{w}(\Gamma)\, \delta(\hat{\Psi}_{\Sigma}^{\mathrm{S}}) + \beta f_{\mathrm{eq}}^{w}(\Gamma)\, \delta\hat{\mathscr{E}}(-t) \tag{3.10b}$$

where

$$\hat{\mathscr{E}} = H_{\Sigma}^{\mathrm{S}} - H_{\Sigma}^{\mathrm{P}} = \hat{\Psi}_{\Sigma}^{\mathrm{S}} - \hat{\Psi}_{\Sigma}^{\mathrm{P}} \tag{3.11}$$

is the *surrogate* counterpart of the *factual* energy gap $\hat{\mathscr{U}}$ defined in Eq. (2.7). Furthermore, $\delta\hat{\mathscr{E}}(-t)$ is the result of applying the operator $\exp(-t\mathscr{L}_{w})$ to the dynamical variable $\delta\hat{\mathscr{E}} = \hat{\mathscr{E}} - \langle \hat{\mathscr{E}} \rangle$ [cf. Eq. (3.3b)].

Replacing Eqs. (3.10) in Eq. (3.5a) leads to the important approximation[(34)]

$$f_{\Sigma}^{\mathrm{h}}(\Gamma, t) = f_{\Sigma,\mathrm{eq}}^{\mathrm{S}}(\Gamma) + \beta f_{\mathrm{eq}}^{w}(\Gamma)\, \delta\hat{\mathscr{E}}(-t) \tag{3.12}$$

where $f_{\Sigma,\mathrm{eq}}^{\mathrm{S}}(\Gamma)$ is the surrogate equilibrium distribution function given by Eq. (3.2). Equation (3.12) is the same as Eq. (3.16) of ref. 34 (where it is derived in a different way), and it also underlies the results for the solvation tcf and the steady-state Stokes shift discussed in ref. 33. It is important to note that in this approximation for the solvent distribution function the dynamics is ruled by the propagator $\mathscr{T}_{w}(t)$ of the homogeneous solvent. This explains the descriptive name "homogeneous" approximation (superscript h) for $f_{\Sigma}^{\mathrm{h}}(\Gamma, t)$; it amounts to a partial neglect of the influence of the solute upon the solvent dynamics in its vicinity.[(33, 34)] We note that this limitation is shared by all other quasianalytical theories of solvation dynamics reported to date. As will be discussed in the next section, this has the consequence that the time dependence of the expectation value of a dynamical variable under $f^{\mathrm{h}}_{\Sigma}(\Gamma, t)$ is described by an equilibrium tcf [Eqs. (4.1) and (4.3) below] governed by $\exp(t\mathscr{L}_{\mathrm{w}})$, the time displacement operator of the homogeneous solvent.

We denote the average of a dynamical variable $\hat{\mathscr{G}}$ under $f^{\mathrm{h}}_{\Sigma}(\Gamma, t)$ by $\langle\!\langle \hat{\mathscr{G}}; t \rangle\!\rangle^{\mathrm{h}}$. It is given by an equation similar to Eq. (2.2), but with $\hat{\mathscr{G}}$ and $f^{\mathrm{h}}_{\Sigma}(\Gamma, t)$ replacing, respectively, $\hat{\mathscr{U}}$ and $f(\Gamma, t)$. In view of the interpretation of $\hat{\mathscr{E}}$ as the surrogate counterpart of $\hat{\mathscr{U}}$, we consider

$$\mathscr{S}^{\mathrm{h}}_{\Sigma}(t) \equiv \frac{\langle\!\langle \hat{\mathscr{E}}; t \rangle\!\rangle^{\mathrm{h}} - \langle\!\langle \hat{\mathscr{E}}; \infty \rangle\!\rangle^{\mathrm{h}}}{\langle\!\langle \hat{\mathscr{E}}; 0 \rangle\!\rangle^{\mathrm{h}} - \langle\!\langle \hat{\mathscr{E}}; \infty \rangle\!\rangle^{\mathrm{h}}} \tag{3.13}$$

as the natural surrogate estimate of the solvation tcf $\mathscr{S}(t)$, Eq. (2.4).

4. EXPECTATION VALUES

With Eq. (3.12) we calculate

$$\langle\!\langle \hat{\mathscr{G}}; t \rangle\!\rangle^{\mathrm{h}} = \langle\!\langle \hat{\mathscr{G}} \rangle\!\rangle^{\mathrm{S}} + \beta C_{\mathscr{G}}(t) \tag{4.1}$$

where

$$\langle\!\langle \hat{\mathscr{G}} \rangle\!\rangle^{D} = \int d\Omega\, p(\Omega) \int d\Gamma\, f^{D}_{\Sigma,\mathrm{eq}}(\Gamma) \hat{\mathscr{G}}, \qquad D = \mathrm{P}, \mathrm{S} \tag{4.2}$$

is the expectation value of $\hat{\mathscr{G}}$ under the *linearized* surrogate equilibrium distribution function $f^{D}_{\Sigma,\mathrm{eq}}(\Gamma)$, Eq. (3.2). Furthermore, $C_{\mathscr{G}}(t)$ is the equilibrium tcf

$$C_{\mathscr{G}}(t) = \langle \delta\hat{\mathscr{G}}(t)\, \delta\hat{\mathscr{E}}(0) \rangle = \int d\Omega\, p(\Omega) \int d\Gamma\, f^{\mathrm{w}}_{\mathrm{eq}}(\Gamma) [\exp(t\mathscr{L}_{\mathrm{w}})\, \delta\hat{\mathscr{G}}]\, \delta\hat{\mathscr{E}} \tag{4.3}$$

which depends [through $f^{\mathrm{w}}_{\mathrm{eq}}(\Gamma)$ and the time displacement operator $\exp(t\mathscr{L}_{\mathrm{w}})$] on the Hamiltonian H_{w} of the homogeneous solvent. In Eq. (4.3) $\delta\hat{\mathscr{G}} = \hat{\mathscr{G}} - \langle \hat{\mathscr{G}} \rangle$.

Assuming that $C_{\mathscr{G}}(t)$ vanishes when $t \to \infty$ (ergodicity), it is a simple matter to show from Eqs. (3.2) and (4.1)–(4.3) that

$$\langle\!\langle \hat{\mathscr{G}}; 0 \rangle\!\rangle^{\mathrm{h}} = \langle\!\langle \hat{\mathscr{G}} \rangle\!\rangle^{\mathrm{P}}, \qquad \langle\!\langle \hat{\mathscr{G}}; \infty \rangle\!\rangle^{\mathrm{h}} = \langle\!\langle \hat{\mathscr{G}} \rangle\!\rangle^{\mathrm{S}} \tag{4.4}$$

We are now in position to derive a convenient expression for the surrogate estimate $\mathscr{S}^{\mathrm{h}}_{\Sigma}(t)$ of the solvation tcf, Eq. (3.13). Thus, using Eqs. (4.1)–(4.4) with $\hat{\mathscr{G}} = \hat{\mathscr{E}}$, the surrogate energy gap, we obtain(33, 34)

$$\mathscr{S}^{\mathrm{h}}_{\Sigma}(t) = \frac{C_{\mathscr{E}}(t)}{C_{\mathscr{E}}(0)} = \frac{\langle \delta\hat{\mathscr{E}}(t)\, \delta\hat{\mathscr{E}}(0) \rangle}{\langle \delta\hat{\mathscr{E}}(0)\, \delta\hat{\mathscr{E}}(0) \rangle} \tag{4.5}$$

This result resembles the familiar linear response approximation $\mathscr{X}^D(t)$ to the solvation tcf $\mathscr{X}(t)$, namely a normalized equilibrium tcf of the factual energy gap $\hat{\mathscr{U}}$ which may be calculated under equilibrium molecular dynamics computer simulations.$^{(20, 23, 25, 26, 31)}$ However, in contrast with the homogeneous estimate $\mathscr{X}^h_\Sigma(t)$, the tcf in the factual estimate $\mathscr{X}^D(t)$ is governed by the solvent Hamiltonian H^D [cf. Eq. (2.5)] that incorporates the bare field of the solute in state D; in the approximation of Eq. (4.5) the influence of the solute enters in the dynamical variable $\hat{\mathscr{E}}$ in a time-independent form.

From Eqs. (4.1) and (4.4) it also follows that if we choose the renormalized solute–solvent couplings $\hat{\Psi}^{\rm P}_\Sigma$ and $\hat{\Psi}^{\rm S}_\Sigma$ such that the equation

$$\langle\!\langle \hat{\mathscr{G}} \rangle\!\rangle^D = \langle \hat{\mathscr{G}} \rangle^D, \qquad D = \mathrm{P, S} \tag{4.6}$$

is satisfied for a *selected* dynamical variable $\hat{\mathscr{G}}$, then the surrogate expectation value $\langle\!\langle \hat{\mathscr{G}}; t \rangle\!\rangle^{\rm h}$ will coincide with the factual correct expectation value $\langle \hat{\mathscr{G}}; t \rangle$ both at $t = 0$ and at $t = \infty$:

$$\langle\!\langle \hat{\mathscr{G}}; 0 \rangle\!\rangle^{\rm h} = \langle \hat{\mathscr{G}}; 0 \rangle = \langle \hat{\mathscr{G}} \rangle^{\rm P}, \qquad \langle\!\langle \hat{\mathscr{G}}; \infty \rangle\!\rangle^{\rm h} = \langle \hat{\mathscr{G}}; \infty \rangle = \langle \hat{\mathscr{G}} \rangle^{\rm S} \tag{4.7}$$

In Eqs. (4.6) and (4.7) we have

$$\langle \hat{\mathscr{G}} \rangle^D = \int d\Omega\, p(\Omega) \int d\Gamma\, f^D_{\rm eq}(\Gamma) \hat{\mathscr{G}} \tag{4.8}$$

where $f^D_{\rm eq}(\Gamma) \sim \exp(-\beta H^D)$ is the equilibrium distribution function of the solvent in the *bare* field of the solute at state D [cf. Eq. (2.5)].

For those dynamical variables $\hat{\mathscr{G}}$ that satisfy Eq. (4.6) we may write Eq. (4.1) in the alternative and remarkable form

$$\langle\!\langle \hat{\mathscr{G}}; t \rangle\!\rangle^{\rm h} = \langle \hat{\mathscr{G}} \rangle^{\rm S} + [\langle \hat{\mathscr{G}} \rangle^{\rm P} - \langle \hat{\mathscr{G}} \rangle^{\rm S}]\, \Phi_{\mathscr{G}}(t) \tag{4.9a}$$

where

$$\Phi_{\mathscr{G}}(t) \equiv C_{\mathscr{G}}(t)/C_{\mathscr{G}}(0) \tag{4.9b}$$

Although Eqs. (4.9) describe the evolution of $\langle\!\langle \hat{\mathscr{G}}; t \rangle\!\rangle^{\rm h}$ through the *equilibrium* tcf $\Phi_{\mathscr{G}}(t)$ (in the same spirit as linear response theory), the fact that the surrogate energy gap $\hat{\mathscr{E}}$ that enters in $\Phi_{\mathscr{G}}(t)$ is defined as the difference between the two renormalized interaction energies $\hat{\Psi}^D_\Sigma$ gives Eqs. (4.9) a flavor of *nonlinear* response. At least Eqs. (4.9) recover the correct (and not necessarily linearly related) values of the expectation value of $\hat{\mathscr{G}}$ at $t = 0$ and $t = \infty$, while at intermediate times they interpolate according to an equilibrium tcf involving a renormalized dynamical variable.

At this point we still have to establish the molecular expressions for the renormalized solute–solvent interactions $\hat{\Psi}^D_\Sigma$. From Eq. (4.4) we concluded that the theory will give the correct values $\langle\langle \hat{\mathscr{G}}; 0 \rangle\rangle^{\mathrm{h}} = \langle \hat{\mathscr{G}}; 0 \rangle$ and $\langle\langle \hat{\mathscr{G}}; \infty \rangle\rangle^{\mathrm{h}} = \langle \hat{\mathscr{G}}; \infty \rangle$ for a dynamical variable $\hat{\mathscr{G}}$ if we choose $\hat{\Psi}^D_\Sigma$ such that Eqs. (4.6) are satisfied. This suggests a method for specifying the renormalized interactions,(34) namely (i) to specify a functional form of the renormalized interactions $\hat{\Psi}^D_\Sigma$ and (ii) to choose the special dynamical variables $\hat{\mathscr{G}}$ for which Eq. (4.6) is required.

In previous work(33, 34) we implemented one such renormalization scheme based on the solvent polarization charge density at point **r** relative to the solute site λ

$$\hat{\rho}_{\lambda,\mu}(\mathbf{r}) = \sum_{aj} q_j \delta(\mathbf{r} - \mathbf{r}_{\lambda,aj}) \tag{4.10}$$

as the special dynamical variable $\hat{\mathscr{G}}$, together with renormalized solute–solvent interactions $\hat{\Psi}^D_\Sigma$ of the form

$$\hat{\Psi}^D_{\Sigma,\mu} = \sum_\lambda \int d^3\mathbf{r}\, \hat{\rho}_{\lambda,\mu}(\mathbf{r})\, \varphi^D_{\Sigma,\lambda}(\mathbf{r}), \qquad D = \mathrm{P, S} \tag{4.11}$$

expressed in terms of *renormalized* electrostatic potentials $\varphi^D_{\Sigma,\lambda}(\mathbf{r})$ due to an *effective* charge density of the solute [cf. Eq. (6.10) below]. With $\hat{\rho}_{\lambda,\mu}(\mathbf{r})$ in the role of $\hat{\mathscr{G}}$, Eq. (4.6) gives

$$\langle\langle \hat{\rho}_{\lambda,\mu}(\mathbf{r}) \rangle\rangle^D = \langle \hat{\rho}_{\lambda,\mu}(\mathbf{r}) \rangle^D = \rho \sum_j q_j h^D_{\lambda j}(r)$$

which is the average solvent polarization charge density at a distance r from the solute site λ when the solute is in electronic state D. As shown in refs. 33 and 34, this form of Eq. (4.6) (for every site λ) is sufficient to fix the identity of the renormalized electrostatic potentials $\varphi^D_{\Sigma,\lambda}(\mathbf{r})$ of Eq. (4.11). This procedure led to an accurate theory of solvation dynamics.(33, 34)

5. SITE NUMBER DENSITY FORMULATION

5.1. Dynamical Variables

Here we investigate an alternative renormalization based on the site number densities of the solvent $\hat{n}_{\lambda,j}(\mathbf{r})$ [cf. Eq. (5.2) below] rather than on the polarization charge density $\hat{\rho}_{\lambda,\mu}(\mathbf{r})$. Correspondingly, we choose to express the renormalized solute–solvent interactions $\hat{\Psi}^D_\Sigma$ in the form [compare with Eq. (4.11)]

$$\hat{\Psi}^D_\Sigma = \sum_\lambda \sum_j \int d^3\mathbf{r}\, \hat{n}_{\lambda,j}(\mathbf{r})\, \phi^D_{\Sigma,\lambda j}(\mathbf{r}) \tag{5.1}$$

in terms of the microscopic solvent site number density of type j at position $\mathbf{r}$ relative to site λ of the solute

$$\hat{n}_{\lambda,j}(\mathbf{r}) = \sum_a \delta(\mathbf{r} - \mathbf{r}_{\lambda,aj}) \tag{5.2}$$

and renormalized pair interactions $\phi^D_{\Sigma,\lambda j}(\mathbf{r})$ that need to be determined. The sum in Eq. (5.2) is carried over all solvent molecules. It is convenient to write $\hat{n}_{\lambda,j}(\mathbf{r})$ as

$$\hat{n}_{\lambda,j}(\mathbf{r}) = \langle \hat{n}_{\lambda,j}(\mathbf{r}) \rangle + \delta\hat{n}_{\lambda,j}(\mathbf{r}), \qquad \langle \hat{n}_{\lambda,j}(\mathbf{r}) \rangle = \rho \tag{5.3}$$

where $\delta\hat{n}_{\lambda,j}(\mathbf{r})$ measures the fluctuations with respect to the average number density ρ of the homogeneous solvent. Note that in writing $\langle \hat{n}_{\lambda,j}(\mathbf{r}) \rangle = \rho$ we have considered the sites of a solvent molecule as different or distinguishable.

With Eq. (5.3), $\hat{\Psi}^D_\Sigma$ given by Eq. (5.1) becomes

$$\hat{\Psi}^D_\Sigma = \langle \hat{\Psi}^D_\Sigma \rangle + \delta(\hat{\Psi}^D_\Sigma) \tag{5.4}$$

where

$$\langle \hat{\Psi}^D_\Sigma \rangle = \sum_\lambda \sum_j \rho \int d^3\mathbf{r}\, \phi^D_{\Sigma,\lambda j}(\mathbf{r}) \tag{5.5a}$$

and

$$\delta(\hat{\Psi}^D_\Sigma) = \hat{\Psi}^D_\Sigma - \langle \hat{\Psi}^D_\Sigma \rangle = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \sum_\lambda \sum_j \delta\hat{n}_{\lambda,j}(\mathbf{k})\, \phi^D_{\Sigma,\lambda j}(-\mathbf{k}) \tag{5.5b}$$

In the second equality $\delta(\hat{\Psi}^D_\Sigma)$ is written in terms of the Fourier transform of the renormalized pair interaction $\phi^D_{\Sigma,\lambda j}(\mathbf{r})$

$$\phi^D_{\Sigma,\lambda j}(\mathbf{k}) = \int d^3\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} \phi^D_{\Sigma,\lambda j}(\mathbf{r}) \tag{5.6a}$$

and the Fourier component of the fluctuating part of the microscopic number density

$$\delta\hat{n}_{\lambda,j}(\mathbf{k}) = \sum_a e^{i\mathbf{k}\cdot\mathbf{r}_{\lambda,aj}} - (2\pi)^3 \rho\delta(\mathbf{k}) \tag{5.6b}$$

Because of the appearance of the Dirac delta function, and noting that $\mathbf{r}_{\lambda,aj}=\mathbf{r}_{aj}-\mathbf{r}_{\lambda}$, we may equally well write the right-hand side of the last equation in the more convenient form

$$\delta\hat{n}_{\lambda,j}(\mathbf{k})=e^{-i\mathbf{k}\cdot\mathbf{r}_{\lambda}}\left[\left(\sum_{a}e^{i\mathbf{k}\cdot\mathbf{r}_{aj}}\right)-(2\pi)^{3}\,\rho\,\delta(\mathbf{k})\right]=e^{-i\mathbf{k}\cdot\mathbf{r}_{\lambda}}\,\delta\hat{n}_{j}(\mathbf{k}) \tag{5.7}$$

The second equality defines $\delta\hat{n}_j(\mathbf{k})$.

5.2. Renormalized Pair Interactions

We now turn to the determination of the $\phi^{D}_{\Sigma,\lambda j}(\mathbf{k})$ using the prescription discussed at the end of Section 4. As the special dynamical variable $\hat{\mathscr{G}}$ for which Eq. (4.6) is enforced we choose $\delta\hat{n}_{\lambda,j}(\mathbf{k})$. Thus, for every λ, we require that

$$\langle\!\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\rangle\!\rangle^{D}=\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\rangle^{D}=\rho h^{D}_{\lambda j}(k) \tag{5.8}$$

The second equality follows from the explicit evaluation of the factual average $\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\rangle^{D}$; here $h^{D}_{\lambda j}(k)$ is the Fourier transform of the (solute site λ)–(solvent site j) equilibrium pair correlation function $h^{D}_{\lambda j}(r)$ when the solute has the state D charge distribution.

To evaluate the left-hand member of Eq. (5.8) we use Eq. (4.2) with $\hat{\mathscr{G}}=\delta\hat{n}_{\lambda,j}(\mathbf{k})$ and $f^{D}_{\Sigma,\mathrm{eq}}(\Gamma)$ defined in Eq. (3.2). After noting that $\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\rangle=0$, we have

$$\begin{aligned}\langle\!\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\rangle\!\rangle^{D}&=-\beta\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\,\delta(\hat{\Psi}^{D}_{\Sigma})\rangle\\&=-\frac{\beta}{(2\pi)^{3}}\int d^{3}\mathbf{k}'\sum_{\lambda'}\sum_{l}\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\,\delta\hat{n}_{\lambda',l}(\mathbf{k}')\rangle\,\phi^{D}_{\Sigma,\lambda' l}(-\mathbf{k}')\end{aligned} \tag{5.9}$$

where in the second equality we have used Eq. (5.5b). For the static average, using Eqs. (3.3a) and (5.7), we evaluate

$$\begin{aligned}\langle\delta\hat{n}_{\lambda,j}(\mathbf{k})\,\delta\hat{n}_{\lambda',l}(\mathbf{k}')\rangle&=\langle e^{-i\mathbf{k}\cdot\mathbf{r}_{\lambda}}e^{-i\mathbf{k}'\cdot\mathbf{r}_{\lambda'}}\rangle_{\Omega}\,\langle\delta\hat{n}_{j}(\mathbf{k})\,\delta\hat{n}_{l}(\mathbf{k}')\rangle\\&=(2\pi)^{3}\,\delta(\mathbf{k}+\mathbf{k}')\,S_{jl}(k)\,\omega_{\lambda\lambda'}(k)\end{aligned} \tag{5.10}$$

In the second equality

$$S_{jl}(k)=\left\{\frac{1}{V}\langle\delta\hat{n}_{j}(\mathbf{k})\,\delta\hat{n}_{l}(-\mathbf{k})\rangle\right\}_{\infty} \tag{5.11}$$

is the static site–site structure factor of the homogeneous solvent, while

$$\omega_{\lambda\lambda'}(k)=\langle e^{-i\mathbf{k}\cdot(\mathbf{r}_{\lambda}-\mathbf{r}_{\lambda'})}\rangle_{\Omega}=\int d\Omega\;p(\Omega)\,e^{-i\mathbf{k}\cdot(\mathbf{r}_{\lambda}-\mathbf{r}_{\lambda'})} \tag{5.12}$$

is the intramolecular site–site correlation function of the solute.(39–41) To derive the second equality of Eq. (5.10) we noticed that the translational invariance of the homogeneous solvent leads to the identities(42)

$$\begin{aligned}\langle \hat{a}(\mathbf{k})\,\hat{b}(\mathbf{k}')\rangle &= \langle \hat{a}(\mathbf{k})\,\hat{b}(-\mathbf{k})\rangle\,\delta_{\mathbf{k},\,-\mathbf{k}'}\\ &= (2\pi)^3\,\delta(\mathbf{k}+\mathbf{k}')\left\{\frac{1}{V}\langle \hat{a}(\mathbf{k})\,\hat{b}(-\mathbf{k})\rangle\right\}_{\infty}\end{aligned} \tag{5.13}$$

where $\hat{a}(\mathbf{k})$ and $\hat{b}(\mathbf{k}')$ are, respectively, the Fourier components of wavevectors $\mathbf{k}$ and $\mathbf{k}'$ of the solvent fields $\hat{a}(\mathbf{r})$ and $\hat{b}(\mathbf{r})$. In Eqs. (5.11) and (5.13) $\{\cdots\}_{\infty}$ indicates the thermodynamic limit operation on the quantity inside the braces.

Combining Eqs. (5.9) and (5.10) leads to

$$\langle\!\langle \delta\hat{n}_{\lambda,j}(\mathbf{k})\rangle\!\rangle^{D} = -\beta\sum_{\lambda'}\sum_{l}\omega_{\lambda\lambda'}(k)\,S_{jl}(k)\,\phi^{D}_{\Sigma,\lambda' l}(\mathbf{k}) \tag{5.14}$$

On the other hand, the right-hand side of Eq. (5.8) may be evaluated with the reference interaction site method (RISM) equation for the solute–solvent site–site pair correlation functions $h^{D}_{\lambda j}(k)$.(39, 40, 43) For the solute at infinite dilution in the solvent we have

$$\rho h^{D}_{\lambda j}(k) = \sum_{\lambda'}\sum_{l}\omega_{\lambda\lambda'}(k)\,c^{D}_{\lambda' l}(k)\,S_{lj}(k) \tag{5.15}$$

Note that the solvent–solvent correlation functions (subscripts lj) correspond to the homogeneous fluid, while $c^{D}_{\lambda j}(k)$ is the solute–solvent RISM site–site direct correlation function when the solute is in state D.

Combining Eqs. (5.8), (5.14), and (5.15), we identify the renormalized solute–solvent pair interaction $\phi^{D}_{\Sigma,\lambda j}(\mathbf{k})$ as proportional to the corresponding solute–solvent direct correlation function

$$-\beta\phi^{D}_{\Sigma,\lambda j}(\mathbf{k}) = -\beta\phi^{D}_{\Sigma,\lambda j}(k) = c^{D}_{\lambda j}(k) \tag{5.16}$$

with an equivalent relation in $\mathbf{r}$-space. With this interpretation of $\phi^{D}_{\Sigma,\lambda j}(\mathbf{r})$, the renormalized solute–solvent potential energy of interaction $\hat{\Psi}^{D}_{\Sigma}$ in Eq. (5.1) is the same as in the Gaussian bath theory of Chandler *et al.*(44)

5.3. Solvation Time Correlation Function

Equations (3.11), (5.4), and (5.5) imply for the surrogate energy gap

$$\hat{\mathscr{E}} = \langle\hat{\mathscr{E}}\rangle + \delta\hat{\mathscr{E}} \tag{5.17}$$

where

$$\langle \hat{\mathscr{E}} \rangle = \sum_{\lambda} \sum_{j} \rho \int d^3\mathbf{r}\; \Delta\phi_{\Sigma,\lambda j}(\mathbf{r}) \tag{5.18a}$$

$$\delta\hat{\mathscr{E}} = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \sum_{\lambda} \sum_{j} \delta\hat{n}_{\lambda,j}(\mathbf{k})\, \Delta\phi_{\Sigma,\lambda j}(-\mathbf{k}) \tag{5.18b}$$

The functions $\Delta\phi_{\Sigma,\lambda j}(\mathbf{r}) \equiv \phi^{\mathrm{S}}_{\Sigma,\lambda j}(\mathbf{r}) - \phi^{\mathrm{P}}_{\Sigma,\lambda j}(\mathbf{r})$ play the role of surrogate *driving* agents,(33) and are given by the equation

$$-\beta\, \Delta\phi_{\Sigma,\lambda j}(\mathbf{r}) = -\beta\, \Delta\phi_{\Sigma,\lambda j}(r) = \Delta c_{\lambda j}(r) \tag{5.19}$$

in terms of $\Delta c_{\lambda j}(r) \equiv c^{\mathrm{S}}_{\lambda j}(r) - c^{\mathrm{P}}_{\lambda j}(r)$.

With Eq. (5.18b) we calculate for $C_{\mathscr{E}}(t) = \langle \delta\hat{\mathscr{E}}(t)\, \delta\hat{\mathscr{E}}(0) \rangle$ in Eq. (4.5)

$$\begin{aligned} C_{\mathscr{E}}(t) = \frac{1}{(2\pi)^6} \int d^3\mathbf{k}\, d^3\mathbf{k}' \sum_{\lambda j} \sum_{\lambda' l} \langle \delta\hat{n}_{\lambda,j}(\mathbf{k}, t)\, \delta\hat{n}_{\lambda',l}(\mathbf{k}') \rangle \\ \times \Delta\phi_{\Sigma,\lambda j}(-\mathbf{k})\, \Delta\phi_{\Sigma,\lambda' l}(-\mathbf{k}') \end{aligned} \tag{5.20}$$

where the dynamic density tcf $\langle \delta\hat{n}_{\lambda,j}(\mathbf{k}, t)\, \delta\hat{n}_{\lambda',l}(\mathbf{k}') \rangle$ is defined under the Hamiltonian H_{w} of the homogeneous solvent. By applying the same steps as in Eq. (5.10) we obtain

$$\langle \delta\hat{n}_{\lambda,j}(\mathbf{k}, t)\, \delta\hat{n}_{\lambda',l}(\mathbf{k}') \rangle = (2\pi)^3\, \delta(\mathbf{k}+\mathbf{k}')\, F_{jl}(k, t)\, \omega_{\lambda\lambda'}(k) \tag{5.21}$$

where

$$F_{jl}(k, t) = \left\{ \frac{1}{V} \langle \delta\hat{n}_j(\mathbf{k}, t)\, \delta\hat{n}_l(-\mathbf{k}) \rangle \right\}_{\infty} \tag{5.22}$$

is the dynamic tcf of the atomic site densities in the homogeneous solvent.(45) The initial value $C_{\mathscr{E}}(0)$ of the surrogate energy gap tcf is obtained from Eqs. (5.20) and (5.21) and noting that $F_{jl}(k, t=0) = S_{jl}(k)$ [cf. Eq. (5.11)]. Therefore, in the renormalization scheme based on the site number densities, we derive for the surrogate estimate $\mathscr{X}^h_{\Sigma}(t)$ of the solvation tcf

$$\mathscr{X}^h_{\Sigma}(t) = \frac{\int_0^\infty dk\, k^2 \sum_{jl} F_{jl}(k, t)\, \mathscr{B}_{\Sigma,jl}(k)}{\int_0^\infty dk\, k^2 \sum_{jl} S_{jl}(k)\, \mathscr{B}_{\Sigma,jl}(k)} \tag{5.23}$$

In this approximation all the details of the solute–solvent interactions are incorporated in the static coupling functions

$$\mathscr{B}_{\Sigma,jl}(k) = \sum_{\lambda\lambda'} \omega_{\lambda\lambda'}(k)\, \Delta\phi_{\Sigma,\lambda j}(k)\, \Delta\phi_{\Sigma,\lambda' l}(k) \tag{5.24}$$

through the surrogate driving agents $\Delta\phi_{\Sigma,\lambda j}(\mathbf{r})$ given in Eq. (5.19). The time dependence, on the other hand, follows from the functions $F_{jl}(k, t)$ of the homogeneous solvent. Equations (5.23) and (5.24) are new results of this work.

The practical implementation of Eq. (5.23) requires the calculation of the static coupling functions $\mathscr{B}_{\Sigma,jl}(k)$, which is no more difficult than the calculation of the coupling function $\mathscr{B}_{\Sigma}(k)$ of the dielectric theory(33, 34) [cf. Eq. (6.17) below]. Equation (5.23) also requires the knowledge of the tcf's $F_{jl}(k, t)$ of the homogeneous solvent, which unfortunately are not easy to calculate. To our knowledge, only the site–site Smoluchowski–Vlasov theory(45) is capable of estimating these functions, but in its current form, only within the diffusion approximation for the dynamics.

6. POLARIZATION CHARGE DENSITY FORMULATION

6.1. Dynamical Variables and Renormalized Electrostatic Potentials

In this section we consider the relation between the renormalized interactions $\hat{\Psi}^D_{\Sigma}$ of the preceding section and the renormalized dielectric theory, based on Eqs. (4.10) and (4.11), presented in previous reports.(33, 34) For this purpose it is convenient to introduce the projection operators

$$\mathscr{P}^{\mathbf{k}}_{\lambda,\mu}(\cdots) = (\ldots, \hat{\rho}_{\lambda,\mu}(\mathbf{k})^*)(\hat{\rho}_{\lambda,\mu}(\mathbf{k}), \hat{\rho}_{\lambda,\mu}(\mathbf{k})^*)^{-1}\, \hat{\rho}_{\lambda,\mu}(\mathbf{k}) \tag{6.1}$$

and $\mathscr{Q}^{\mathbf{k}}_{\lambda,\mu} = 1 - \mathscr{P}^{\mathbf{k}}_{\lambda,\mu}$. Here

$$\hat{\rho}_{\lambda,\mu}(\mathbf{k}) = \sum_{aj} q_j e^{i\mathbf{k}\cdot\mathbf{r}_{\lambda,aj}} \tag{6.2}$$

is the Fourier component of the solvent polarization charge density $\hat{\rho}_{\lambda,\mu}(\mathbf{r})$ given in Eq. (4.10). A more useful representation is

$$\hat{\rho}_{\lambda,\mu}(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}_{\lambda}} \sum_{aj} q_j e^{i\mathbf{k}\cdot\mathbf{r}_{aj}} = e^{-i\mathbf{k}\cdot\mathbf{r}_{\lambda}}\hat{\rho}_{\mu}(\mathbf{k}) \tag{6.3}$$

where the second equality defines the Fourier component of the solvent polarization charge density relative to an arbitrary reference frame.

In Eq. (6.1) we have introduced the scalar product

$$\cdot\ (\hat{a}(\mathbf{k}), \hat{b}(\mathbf{k})^*) = \left\{\frac{1}{V}\langle \hat{a}(\mathbf{k})\, \hat{b}(-\mathbf{k})\rangle\right\}_{\infty} \tag{6.4}$$

in terms of the homogeneous solvent average of Eq. (3.3a). It is not difficult to show that $\langle \hat{\rho}_{\lambda,\mu}(\mathbf{k})\rangle = \langle \hat{\rho}_{\mu}(\mathbf{k})\rangle = 0$.

With the help of the operators $\mathscr{P}^{\mathbf{k}}_{\lambda,\mu}$ and $\mathscr{Q}^{\mathbf{k}}_{\lambda,\mu}$ we can dissect $\delta\hat{n}_{\lambda,j}(\mathbf{k})$ into a component *proportional* to the fluctuating polarization charge density $\hat{\rho}_{\lambda,\mu}(\mathbf{k})$ and a component that is *orthogonal* to it,

$$\delta\hat{n}_{\lambda,j}(\mathbf{k}) = (\mathscr{P}^{\mathbf{k}}_{\lambda,\mu} + \mathscr{Q}^{\mathbf{k}}_{\lambda,\mu})\,\delta\hat{n}_{\lambda,j}(\mathbf{k}) = \vartheta_j(k)\,\hat{\rho}_{\lambda,\mu}(\mathbf{k}) + \delta\hat{\zeta}_{\lambda,j}(\mathbf{k}) \tag{6.5}$$

The magnitude of the component along $\hat{\rho}_{\lambda,\mu}(\mathbf{k})$, the "dielectric part" (subscript μ), is measured by the charge number factor

$$\vartheta_j(k) \equiv (\delta\hat{n}_{\lambda,j}(\mathbf{k}), \hat{\rho}_{\lambda,\mu}(\mathbf{k})^*)(\hat{\rho}_{\lambda,\mu}(\mathbf{k}), \hat{\rho}_{\lambda,\mu}(\mathbf{k})^*)^{-1} \tag{6.6a}$$

which, after using Eqs. (5.7), (6.3), and (6.4), may be expressed in terms of the equilibrium structure functions of the homogeneous solvent[33, 34]

$$\vartheta_j(k) = \frac{\sum_i q_i[\omega_{ij}(k) + \rho h_{ij}(k)]}{\sum_i \sum_l q_i q_l[\omega_{il}(k) + \rho h_{il}(k)]} \tag{6.6b}$$

For the orthogonal part (subscript ζ) we have

$$\delta\hat{\zeta}_{\lambda,j}(\mathbf{k}) = \mathscr{Q}^{\mathbf{k}}_{\lambda,\mu}\,\delta\hat{n}_{\lambda,j}(\mathbf{k}) = \delta\hat{n}_{\lambda,j}(\mathbf{k}) - \vartheta_j(k)\,\hat{\rho}_{\lambda,\mu}(\mathbf{k}) \tag{6.7}$$

It is important to note that the μ and ζ components of $\delta\hat{n}_{\lambda,j}(\mathbf{k})$ are mutually orthogonal with respect to the scalar product of Eq. (6.4) only when they are evaluated at the same instant.

The separation of $\delta\hat{n}_{\lambda,j}(\mathbf{k})$ according to Eq. (6.5) directly leads to a similar decomposition of the renormalized solute–solvent potential energy of interaction, Eq. (5.5b),

$$\delta(\hat{\Psi}^D_\Sigma) = \delta(\hat{\Psi}^D_{\Sigma,\mu}) + \delta(\hat{\Psi}^D_{\Sigma,\zeta}) \tag{6.8}$$

where

$$\delta(\hat{\Psi}^D_{\Sigma,\mu}) = \frac{1}{(2\pi)^3}\int d^3\mathbf{k} \sum_\lambda \hat{\rho}_{\lambda,\mu}(\mathbf{k})\,\varphi^D_{\Sigma,\lambda}(-\mathbf{k}) \tag{6.9a}$$

$$\delta(\hat{\Psi}^D_{\Sigma,\zeta}) = \frac{1}{(2\pi)^3}\int d^3\mathbf{k} \sum_\lambda \sum_j \delta\hat{\zeta}_{\lambda,j}(\mathbf{k})\,\phi^D_{\Sigma,\lambda j}(-\mathbf{k}) \tag{6.9b}$$

Note that in this approach the polarization part $\delta(\hat{\Psi}^D_{\Sigma,\mu})$ is naturally expressed in terms of the Fourier transform $\varphi^D_{\Sigma,\lambda}(\mathbf{k})$ of the renormalized electrostatic potentials $\varphi^D_{\Sigma,\lambda}(\mathbf{r})$ at position $\mathbf{r}$ relative to site λ of the solute in state D. The electrostatic potentials $\varphi^D_{\Sigma,\lambda}(\mathbf{r})$ are related to the renormalized pair interactions $\phi^D_{\Sigma,\lambda j}(\mathbf{r})$ by the relation

$$-\beta\varphi^D_{\Sigma,\lambda}(\mathbf{k}) = -\beta\sum_j \vartheta_j(k)\,\phi^D_{\Sigma,\lambda j}(\mathbf{k}) = \sum_j \vartheta_j(k)\,c^D_{\lambda j}(k) \tag{6.10}$$

where in the second equality we have used Eq. (5.16). Applying Parseval's theorem, we see that Eq. (6.9a) is the same as Eq. (4.11), which is the basis for the renormalized dielectric formulation developed in refs. 33 and 34. The equivalence is completed with Eq. (6.10) for the interpretation of the renormalized electrostatic potentials $\varphi^{D}_{\Sigma,\lambda}(\mathbf{k})$.(33, 34)

6.2. Solvation Time Correlation Function

It follows from Eqs. (6.8) and (6.9) that the surrogate energy gap $\hat{\mathscr{E}}$, Eqs. (5.17) and (5.18), also separates into two components:

$$\hat{\mathscr{E}} = \langle \hat{\mathscr{E}} \rangle + \delta\hat{\mathscr{E}}_{\mu} + \delta\hat{\mathscr{E}}_{\zeta} \tag{6.11}$$

where

$$\delta\hat{\mathscr{E}}_{\mu} = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \sum_{\lambda} \hat{\rho}_{\lambda,\mu}(\mathbf{k})\, \Delta\varphi_{\Sigma,\lambda}(-\mathbf{k}) \tag{6.12a}$$

and

$$\delta\hat{\mathscr{E}}_{\zeta} = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \sum_{\lambda} \sum_{j} \delta\hat{\zeta}_{\lambda,j}(\mathbf{k})\, \Delta\phi_{\Sigma,\lambda j}(-\mathbf{k}) \tag{6.12b}$$

In the polarization part $\delta\hat{\mathscr{E}}_{\mu}$ we have [compare with Eq. (5.19)]

$$-\beta\, \Delta\varphi_{\Sigma,\lambda}(\mathbf{k}) = -\beta\, \Delta\varphi_{\Sigma,\lambda}(k) = \sum_{j} \vartheta_j(k)\, \Delta c_{\lambda j}(k) \tag{6.13}$$

The result for the surrogate estimate $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ of the solvation tcf reported in refs. 33 and 34 [under the notation $\mathscr{X}^{\mathrm{h}}_{\Sigma}(t)$] is recovered from Eq. (4.5) by systematically neglecting in the equations of Section 5.3 the ζ component of the surrogate energy gap, i.e., $\delta\hat{\mathscr{E}} \simeq \delta\hat{\mathscr{E}}_{\mu}$. Thus the surrogate estimate $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ is calculated from the normalized energy gap tcf $C_{\mathscr{E},\mu}(t)/C_{\mathscr{E},\mu}(0)$, where

$$C_{\mathscr{E},\mu}(t) = \langle \delta\hat{\mathscr{E}}_{\mu}(t)\, \delta\hat{\mathscr{E}}_{\mu}(0) \rangle \tag{6.14}$$

With Eq. (6.12a) and repeating the steps leading to Eq. (5.23) we find(33, 34)

$$\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t) = \frac{\int_0^\infty dk\, k^2 C_{\mu}(k, t)\, \mathscr{B}_{\Sigma}(k)}{\int_0^\infty dk\, k^2 S_{\mu}(k)\, \mathscr{B}_{\Sigma}(k)} \tag{6.15}$$

The time dependence of $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ is governed by the polarization charge tcf of the homogeneous solvent

$$C_{\mu}(k, t) = \left\{ \frac{1}{V} \langle \hat{\rho}_{\mu}(\mathbf{k}, t)\, \hat{\rho}_{\mu}(-\mathbf{k}) \rangle \right\}_{\infty} \tag{6.16}$$

which is functionally equivalent to the frequency- and wavevector-dependent longitudinal dielectric function of the homogeneous solvent.(15, 35–37) Correspondingly, $S_\mu(k) \equiv C_\mu(k, t=0)$ is functionally equivalent to the static longitudinal dielectric function of the solvent.(15, 46) In $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ the effects of the solute–solvent interactions appear in the static coupling function(33, 34)

$$\mathscr{B}_\Sigma(k) = \sum_{\lambda\lambda'} \omega_{\lambda\lambda'}(k)\, \Delta\varphi_{\Sigma,\lambda}(k)\, \Delta\varphi_{\Sigma,\lambda'}(k) \tag{6.17}$$

through the renormalized driving agents $\Delta\varphi_{\Sigma,\lambda}(k)$, Eq. (6.13).

A complementary interpretation of $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ is provided by the equation

$$\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t) \equiv \frac{\langle\langle \delta\hat{\mathscr{E}}_\mu; t\rangle\rangle^{\mathrm{h}}_\mu - \langle\langle \delta\hat{\mathscr{E}}_\mu; \infty\rangle\rangle^{\mathrm{h}}_\mu}{\langle\langle \delta\hat{\mathscr{E}}_\mu; 0\rangle\rangle^{\mathrm{h}}_\mu - \langle\langle \delta\hat{\mathscr{E}}_\mu; \infty\rangle\rangle^{\mathrm{h}}_\mu} \tag{6.18}$$

where $\langle\langle \delta\hat{\mathscr{E}}_\mu; t\rangle\rangle^{\mathrm{h}}_\mu$ denotes the average of the polarization part of the surrogate energy gap over a different surrogate nonequilibrium distribution function $f^{\mathrm{h}}_{\Sigma,\mu}(\Gamma, t)$. The latter is obtained by repeating the derivation in Section 3 using the form $\hat{\Psi}^D_{\Sigma,\mu}$, Eq. (4.11), for the renormalized solute–solvent interactions. The derivation of $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ in ref. 34 was obtained by this method.

7. APPLICATIONS OF THE DIELECTRIC THEORY

The accurate implementation of the surrogate estimate $\mathscr{X}^{\mathrm{h}}_{\Sigma}(t)$, Eq. (5.23), must wait for improvements in the theory of the site number density tcf's $F_{jl}(k, t)$ of the homogeneous solvent.(45, 47) For this reason in this section we only present results for the surrogate estimate $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ of the solvation tcf. Two examples are considered: the solvation dynamics of an ion in water,(33, 34) and the solvation dynamics of a family of benzenelike solutes in acetonitrile.

7.1. Methodology

In all cases considered here, the intermolecular potential function between sites i and j of two different molecules (solute–solvent or solvent–solvent) consists of electrostatic and Lennard–Jones (LJ) terms

$$u_{ij}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{q_i q_j}{r} \tag{7.1}$$

The LJ interaction parameters between unlike sites are evaluated with the familiar Lorentz–Berthelot combining rules.

To evaluate the dynamic and static aspects of solvation required by the dielectric theory of Section 6 we need estimates for the pure solvent dynamics and structure, as represented by $C_\mu(k, t)$ and its initial value $S_\mu(k)$. In all cases the required solute–solvent and solvent–solvent structure functions are calculated with the extended reference interaction site method (XRISM).(43)

The tcf $C_\mu(k, t)$ is calculated using the reference memory function approximation (RMFA) method.(15, 35–37) This method identifies the normalized first memory function(48) of $C_\mu(k, t)$ with the normalized first memory function of the known tcf $\langle X(t)\, X(0)\rangle$ of a reference dynamical variable X, thus providing an approximate relation(15, 35–37) between $C_\mu(k, t)$ and the reference tcf $\langle X(t)\, X(0)\rangle$. Following the proposal of Fried and Mukamel,(13) we take as the reference dynamical variable $X = \{\hat{\rho}_\mu(\mathbf{k})/ik\}_{k=0} = \hat{M}_L = \mathbf{e}_k \cdot \sum_a \boldsymbol{\mu}_a$, the total electric polarization in the direction $\mathbf{e}_k$ of the wavevector $\mathbf{k}$ ($\boldsymbol{\mu}_a$ is the dipole moment of a solvent molecule).[7] The tcf $\langle \hat{M}_L(t)\, \hat{M}_L(0)\rangle$ is a known functional of the frequency-dependent dielectric function ε_ω.(49) In our calculations either of these functions is taken from MD simulation results of various solvent models reported in the literature.

7.2. Solvation Dynamics of a Univalent Ion in Water

To illustrate the usefulness of our approach, we compare for the dynamic solvation of an ion in water the surrogate estimate $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$, Eq. (6.15), with the solvation tcf $\mathscr{X}(t)$ calculated by nonequilibrium molecular dynamics (MD), Eq. (2.4). The simulation results are taken from the MD study by Maroncelli and Fleming,(20) who used the ST2 water model of Stillinger and Rahman.(50) Our calculations use the transferable intermolecular potential model TIP4P of water due to Jorgensen and collaborators.(51) The motivation for choosing TIP4P is that a detailed characterization of the frequency-dependent dielectric function ε_ω by MD applied to this water model has been given by Neumann.(52) It provides our input for the calculation of $C_\mu(k, t)$ under the RMFA approximation.(35–37) A further reason is our ability to calculate the structure of this model under XRISM.

In Fig. 1 we compare the predictions of the surrogate theory $\mathscr{X}^{\mathrm{h}}_{\Sigma,\mu}(t)$ and the results of nonequilibrium MD trajectories of Maroncelli and

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[7] As implemented here, the RMFA approximation corresponds to the extension to ISM molecular fluids of the procedure introduced by Fried and Mukamel(13) to calculate the longitudinal dielectric function of a fluid of dipolar hard spheres.

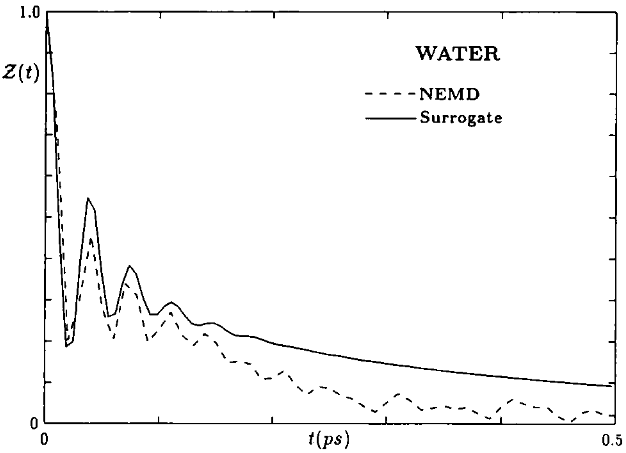

Fig. 1. Solvation time correlation functions for ion solvation in water. The curve NEMD is from MD simulations by Maroncelli and Fleming,(20) while the curve Surrogate is based on the present work. NEMD: Solvation tcf $\mathscr{Z}(t)$ calculated from nonequilibrium MD trajectories corresponding to the P → S transition, Eq. (2.4). Surrogate: Solvation tcf $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ calculated with Eq. (6.15). The Lennard-Jones parameters of the solute are given in the text. t is in units of ps.

Fleming (for a more complete comparison, together with other examples, see refs. 33 and 34). The case considered here corresponds to the one labeled $L0 \rightarrow L+$ (large neutral → large cation) in ref. 20, namely a spherical solute with LJ parameters $\varepsilon/k_{\mathrm{B}} = 2668$ K (where k_{B} is the Boltzmann constant) and $\sigma = 6.975$ Å, which undergoes ionization from $Q^{\mathrm{P}}/e = 0$ to $Q^{\mathrm{S}}/e = 1$ (where e is the proton charge).

As Fig. 1 shows, the theoretical estimate $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ agrees surprisingly well with the nonequilibrium MD response. The surrogate solvation tcf in Fig. 1 displays (i) a very fast initial decay ($\approx 60\%$ of the total decay within 20–30 fs), (ii) a strong oscillatory feature due to the collective librational motion (optical mode) of water (see refs. 36 and 37 and references therein), and (iii) a final slower relaxation of diffusive character.

7.3. Solvation Dynamics of Benzenelike Solutes in Acetonitrile

In this section we report calculations of $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ for a family of "benzenelike" solutes in acetonitrile. The purpose is to examine the effect of the bare charge distribution $n_0^D(\mathbf{r})$ of the solute on the solvation time correlation function.[8]

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[8] The bare charge distribution of the solute in state D has the expression $n_0^D(\mathbf{r}) = \sum_\lambda Q_\lambda^D \delta(\mathbf{r} - \mathbf{r}_\lambda)$.

The solvent is the three-site ISM model of acetonitrile developed by Edwards *et al.*(53) As input for the calculation of $C_\mu(k, t)$ in Eq. (6.15) under the RMFA methodology (cf. Section 7.1), we use the polarization tcf $\langle \hat{M}_L(t)\, \hat{M}_L(0) \rangle$ reported in ref. 53.

The family of solutes studied comprises five models, four of which have 6 interaction sites, while the remaining one has 12 interaction sites. The geometry of the models is that of the benzene molecule, with a united-atom representation of the C–H unit in the case of the 6-site models. For the 6-site solutes, the LJ parameters are taken from the 6-interaction-site model of benzene of Jorgensen and collaborators.(54) For the 12-site solute the LJ parameters are taken from the more recent 12-interaction-site model of benzene developed by Jorgensen and Severance.(55)

In the P state all the solutes have zero partial charges Q_λ^{P}, so that $n_0^{\mathrm{P}}(\mathbf{r}) = 0$. The solutes are labeled after their charge distribution in the S state: localized monopole (lM), delocalized monopole (dM), dipole (D), quadrupole (Q), and octupole (O). A schematic representation of the solutes in the S state is shown in Fig. 2. The labels of the solutes correspond to the first nonzero multipole of the charge distribution $n_0^{\mathrm{S}}(\mathbf{r})$. Note, however, that because the charge distributions have finite size, the higher-order multipoles are nonzero. In the S state the lM model has a partial

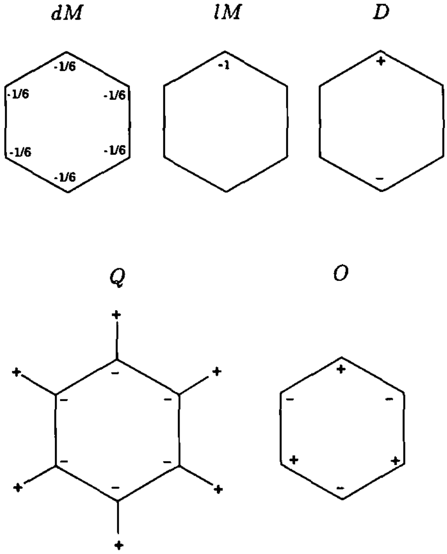

Fig. 2. Charge distribution of the "benzenelike" solutes in the S state. The partial charges Q_λ^{P} of the solutes in the P states are zero. The magnitudes of the partial charges Q_λ^{S} and other specifications of the models are given in the text.

charge $Q^{\mathrm{S}}_1/e = -1$ in site $\lambda = 1$, and zero charge in the other sites, while in the dM model the sites have all the same charge $Q^{\mathrm{S}}_\lambda/e = -1/6 = -0.167$. In the D model $Q^{\mathrm{S}}_1/e = -Q^{\mathrm{S}}_4/e = 0.25$. Finally, the absolute value of the partial charges in the Q and O models is $|Q^{\mathrm{S}}_\lambda/e| = 0.115$ and 0.167, respectively.

In Fig. 3 we present $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ for the P → S transition of the dM, D, Q, and O models. According to the figure, the solvation rate depends markedly on the order of the first nonzero multipole in $\Delta n_0(\mathbf{r}) \equiv n^{\mathrm{S}}_0(\mathbf{r}) - n^{\mathrm{P}}_0(\mathbf{r})$; the solvation is slower with increasing multipole order of $\Delta n_0(\mathbf{r})$. Thus, for the dM model there is a very fast initial decay of $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ (approximately 90% of its initial value within the first 200 fsec), followed by a slower decay that presents pronounced oscillations, for which the librational motion of acetonitrile is responsible.(23, 33, 34) For the D model, $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ presents a slower but still very fast initial decay (approximately 75% in 200 fsec), but the oscillation amplitude is markedly attenuated compared to the oscillations in $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ of the dM model. For the Q and O models $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ decays more slowly (approximately 55 and 45% of the initial value within the first 200 fsec, respectively), while the oscillations have almost disappeared. The ordering, monopole faster than

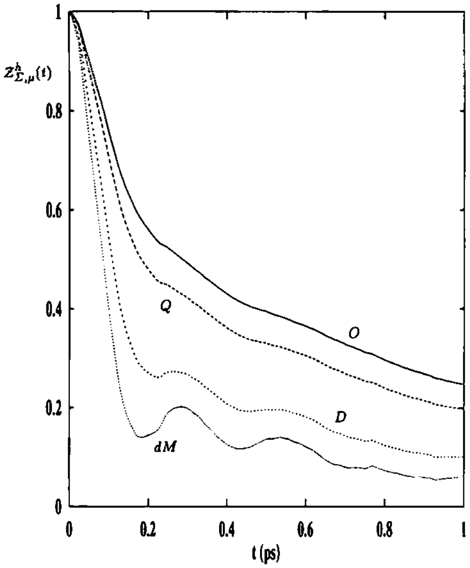

Fig. 3. Surrogate estimate $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ of the solvation time correlation function for the benzenelike solutes in acetonitrile. The curves correspond to the solvation dynamics of the dM, D, Q, and O solutes following the P → S transition. t is in units of ps.

dipole faster than quadrupole faster than octupole, is in agreement with the results for another family of solutes (of different geometry) reported previously.(34)

In Fig. 4 we present results for P → S transitions that complement the results of Fig. 3. Curves dM and lM correspond to the surrogate estimate $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ for the "monopole" solutes. The strong similarity of these curves indicates that the solvation dynamics in acetonitrile is only negligibly affected by the nature, distributed (dM) or localized (lM), of the charge distribution $n^{\mathrm{S}}_0(\mathbf{r})$ of the monopole solutes. Together with Fig. 3, this result suggests that for this family of solutes in acetonitrile, what dominates the solvation response is the *order* of the lowest multipole that contributes to $\Delta n_0(\mathbf{r})$ in the P → S transition. That this is the case is illustrated by the similarity of curves D and dM → lM of Fig. 4. Curve D corresponds to the P → S transition of the D model; it is the same as curve D in Fig. 3. In this transition the multipolar contribution to $\Delta n_0(\mathbf{r})$ of lowest order is the dipolar one. On the other hand, the curve lM → dM corresponds to a 6-site

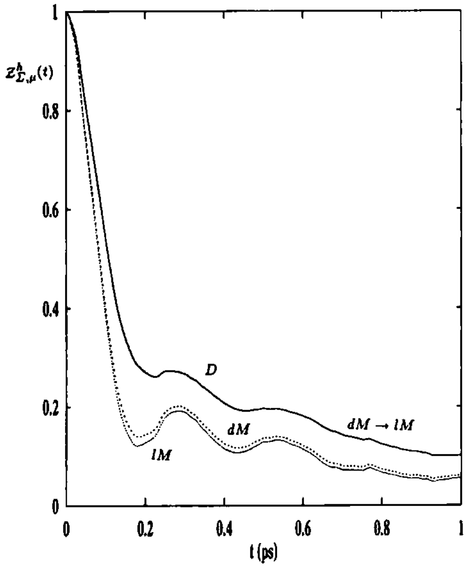

Fig. 4. Surrogate estimate $\mathscr{Z}^{\mathrm{h}}_{\Sigma,\mu}(t)$ of the solvation time correlation function for the benzenelike solutes in acetonitrile. The curves dM and lM correspond to the solvation dynamics following the P → S transition of the DM and lM solutes. Curves D and dM → lM (practically indistinguishable) correspond, respectively, to the P → S transition of the D solute and to a 6-site solute that undergoes a P → S transition from delocalized monopole to localized monopole. See details in the text. *t* is in units of ps.

monopole solute that undergoes a transition from delocalized monopole (with the charge distribution of the dM model) to localized monopole (with the charge distribution of the lM model). Because in such P → S transition both states have the same net charge, the lowest-order multipole contributing to $\Delta n_0(\mathbf{r})$ is again the dipole. Hence we conclude from the results of Figs. 3 and 4 that the solvation dynamics of the benzenelike solutes in acetonitrile is dominated by the lowest-order multipole of the difference function $\Delta n_0(\mathbf{r})$ between the charge distributions of the solute in the P and S states.

8. DISCUSSION

We have presented a generalization of a recently proposed(33, 34) molecular theory of solvation dynamics. Like the polarization charge density formulation,(33, 34) the site number density formulation is capable not only of describing the normalized solvation tcf [cf. Eq. (5.23)], but also of describing the evolution of various ancillary observables needed for a more detailed picture of the dynamic solvation response.(34) Both formulations of the surrogate Hamiltonian theory are also able to quantify the contribution from various regions in the solvent around the solute to the global measures of the solvation response.(34)

The study of such problems in the site number density formulation, however, must wait for further developments in the theory of the dynamics of ISM molecular liquids, so that, for example, the site–site dynamic structure functions $F_{jl}(k, t)$, Eq. (5.22), can be calculated accurately.

A distinctive and important feature of these formulations of the surrogate Hamiltonian theory is that both the solute and the solvent molecules are described in terms of relatively realistic interaction site models. We emphasize that at no point in the development have we appealed to cavity constructs to describe the solute–solvent coupling. In the theory this coupling is treated at a molecular level in terms of the usual structural functions [Eqs. (5.16) and (6.10)] of the theory of fluids.

ACKNOWLEDGMENTS

F.O.R. gratefully acknowledges a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) of Argentina. This material is based upon work supported by the National Science Foundation under grant CHE 9023516.

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