Dipole solvation in dielectrics

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(Received 2 September 2003; accepted 21 October 2003)

This paper presents an exact solution for the free energy of linear solvation of a dipolar solute in an arbitrary dielectric medium with a microscopic spectrum of polarization fluctuations. The solution is given in terms of a wave vector-dependent longitudinal and transverse structure factors of the polarization fluctuations in the pure dielectric. Good agreement with computer simulations of dipole solvation in dipolar and dipolar-quadrupolar liquids is achieved. © 2004 American Institute of Physics. [DOI: 10.1063/1.1633545]

I. INTRODUCTION

Calculation of the energetics of solvation of a dipolar solute in a dense polar solvent is a classical problem of chemical physics and solution chemistry. Thermodynamics of dipole solvation predominantly determines the solvent effect on steady-state optical spectra. The dynamics of solvation shells are significant for transport properties and rotational relaxation, and time-resolved progression of optical lines. A part of the widespread interest in dipole solvation comes from the desire to learn about a complex condensed-phase environment from the alteration of steady-state or time-resolved spectra of dipolar spectral dyes. Among applications of this approach are supercritical solvents, liquid–glass transitions, and heterogeneous systems in biology and surface science. The use of dipolar spectral probes is limited, however, by the assumption that the observed spectral response directly represents a solvent property. In other words, the fundamental requirement for using spectroscopy to probe condensed-phase media is the ability to solve the inverse problem of obtaining solvent characteristics from observed spectra. The absence of an exact route between the thermodynamic parameters of dipole solvation available from spectral analysis and solvent parameters affecting dipole solvation poses a serious limit to all techniques employing dipolar dyes to probe condensed-phase media.

The only currently available exact analytical solution for the chemical potential of solvation $\mu_0$, of a dipolar solute in an arbitrary dielectric material is the expression employing the Onsager solution for the dipolar reaction field

$$ -\mu_0 = \frac{m_0^2}{a^2} \left( \frac{e-1}{2e+1} \right). $$

Here, “0” refers to the solute, s stands for the solvent, $m_0$ is the solute dipole moment, and $a$ is the radius of a spherical cavity cut from the dielectric when a spherical solute is immersed into a solvent. The great advantage of the Onsager solution is that it is applicable to any dielectric characterized by the dielectric constant $e$. The solution directly extends to the time-resolved solvent response by using the frequency-dependent dielectric constant $e(\omega)$, as has been broadly applied to describe solvation dynamics.

Equation (1) applies to a spherical solute with a central point dipole. Extensions to arbitrary shapes and charge distributions are possible within numerical solutions of the Poisson equation with boundary conditions set up by the cavity. There are, however, several major problems with the Onsager solution and, probably, with its extensions within continuum solvation models. First, the cavity radius is not defined, and the assumption that $a$ is equal to the van der Waals or hard-sphere (HS) radius of the solute $R_0$ gives $-\mu_0$, significantly higher than exact values from computer simulations. The chemical potential $\mu_0$, is very sensitive to the radius definition, and no broadly applicable scheme of defining the dielectric cavity has been formulated so far. Second, the formulation relies on the macroscopic dielectric constant as the only solvent property affecting $\mu_0$. No microscopic characteristics of the dielectric are included in the description.

Microscopic theories of solvation do not rely on artificial definitions of the dielectric cavity and bring microscopic properties of the solvent into the formulation. Two basic microscopic approaches to solvation thermodynamics, perturbation expansions and integral equation theories, are currently employed. Perturbation expansions are divergent for polar solvents and must be truncated within some approximate scheme. Stell’s Padé truncation appears to be a successful approximation when applied to dipole solvation. Integral equation theories provide accurate numerical solutions of the corresponding closure relations. Calculations of highly polar solvent are, however, very demanding computationally as they require solving a large set of Ornstein–Zernike equations obtained by expanding the correlation functions in rotational invariants. An exact analytical result for $\mu_0$ is available within the mean-spherical approximation (MSA). But the MSA closure is not accurate when applied to thermodynamic and dielectric properties of model polar solvents. From a more general perspective, all currently available microscopic approaches are strongly dependent on the model used to describe the solvent, and do not provide a general microscopic solution applicable to an arbitrary dielectric.
The goal of the present paper is to formulate an exact, analytical solution for the linear solvation free energy of a dipolar solute in an arbitrary dielectric material characterized by the microscopic spectrum of fluctuations of its dipolar polarization. A general formulation of the problem in terms of a solute of an arbitrary shape with an arbitrary charge distribution in given in Secs. II and III. This formulation may provide a basis for numerical calculations of the solvation thermodynamics. An analytical solution becomes possible for dipolar symmetry of the solute field as is shown in Sec. IV. The paper concludes with the discussion of the results and the comparison to Monte Carlo (MC) simulations of solvation in dipolar–quadrupolar fluids in Sec. V.

II. FORMALISM

The present formulation is limited to the linear response approximation (LRA), in which \( \mu_0 \) is a quadratic function of the solute dipole \( m_0 \), as in Eq. (1). Several equivalent definitions of \( \mu_0 \) can be used within the LRA. We will use the definition in terms of the second cumulant of the solute–solvent interaction potential \( v_{0s} \):

\[
-\mu_0 = \frac{\beta}{2} \langle (\delta v_{0s})^2 \rangle_0 .
\]

Here, \( \langle \ldots \rangle_0 \) stands for the statistical average over the configurations of the solvent in equilibrium with a fictitious solute which has the repulsive potential of the real solute, but bears zero dipole moment (subscript “0” in the statistical average); \( \beta = 1/k_BT \), \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature. In the LRA, the definition given by Eq. (2) is equivalent to two other definitions: \( \mu_0 = \langle v_{0s} \rangle_2 / 2 \) and \( -\mu_0 = \beta \langle (\delta v_{0s})^2 \rangle_2 / 2 \), where \( \langle \ldots \rangle \) stands for the statistical average over the solvent configurations in equilibrium with the solute possessing the dipole \( m_0 \).

In polar solvents, the solute–solvent interaction potential is the interaction of solute’s electric field \( E_0(r) \) with the solvent dipolar polarization \( P(r) \):

\[
v_{0s} = -\int \mathbf{E}_0(r) \cdot \mathbf{P}(r) d\mathbf{r} .
\]

From Eqs. (2) and (3), \( \mu_0 \) can be directly rewritten in the form of the Fourier integral

\[
-\mu_0 = \frac{1}{2} \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{(2\pi)^6} \tilde{E}_0(\mathbf{k}_1) \cdot \mathbf{\chi}(\mathbf{k}_1, \mathbf{k}_2) \cdot \tilde{E}_0(\mathbf{k}_2)^* .
\]

In Eq. (4), \( \tilde{E}_0(\mathbf{k}) \) is the Fourier transform of the solute field taken over the solvent volume \( \Omega \) outside the solute

\[
\tilde{E}_0(\mathbf{k}) = \int_{\Omega} \mathbf{E}_0(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} ,
\]

and \( \tilde{E}_0(\mathbf{k})^* \) stands for its complex conjugate. The response function of the solvent polarization \( \mathbf{\chi} \) is the second-rank tensor calculated on the solvent configurations in equilibrium with the solute hard core excluding the solute from its volume. In terms of the Cartesian components (subscripts \( \alpha, \beta \)) of the fluctuation \( \delta \mathbf{P}(\mathbf{k}) \) of the \( \mathbf{k} \)-space solvent polarization field, \( \mathbf{\chi} \) becomes

\[
\chi_{\alpha\beta}(\mathbf{k}_1, \mathbf{k}_2) = \beta \langle \delta \mathbf{P}_{\alpha}(\mathbf{k}_1) \delta \mathbf{P}_{\beta}(\mathbf{k}_2)^* \rangle_0 .
\]

The calculation of the response function \( \mathbf{\chi} \) for an arbitrary distribution of charge within a molecular solute of arbitrary shape has been a major challenge of linear solvation theories. This problem is still unresolved for a \( \mathbf{k} \)-dependent nonlocal response describing microscopic, molecular fluctuations of polar solvents. The \( k_{1,2} = 0 \) limit for the function \( \mathbf{\chi}(\mathbf{k}_1, \mathbf{k}_2) \) leads to continuum solvation theories when the solution of the problem is sought by solving the Poisson equation with the boundary conditions defined by solute’s molecular shape.

The first approximation which can be adopted for calculations with a nonlocal solvent response is to assume that \( \mathbf{\chi} \) is equal to the response function \( \chi_0 \) of the bulk solvent unperturbed by the solute

\[
\chi(\mathbf{k}_1, \mathbf{k}_2) = \delta_{\mathbf{k}_1, \mathbf{k}_2} \chi_0(\mathbf{k}_1) .
\]

where \( \delta_{\mathbf{k}_1, \mathbf{k}_2} = (2\pi)^3 \delta(\mathbf{k}_1 - \mathbf{k}_2) \) and

\[
\chi_{0\beta}(\mathbf{k}) = \beta \langle \delta \mathbf{P}_\alpha(\mathbf{k}) \delta \mathbf{P}_\beta(\mathbf{k})^* \rangle_0 .
\]

In Eq. (8), \( \langle \ldots \rangle_0 \) stands for the equilibrium statistical average over the configurations of the pure solvent (subscript “s”). If the approximation given by Eq. (7) was correct, it would provide a direct connection between microscopic properties of the bulk solvent and solvation thermodynamics. The dipolar symmetry of the polarization field splits \( \chi_0 \) into two projections corresponding to the axial symmetry of the wave vector \( \mathbf{k} \): longitudinal (parallel to \( \mathbf{k} = \mathbf{k}/|\mathbf{k}| \)) and transverse (perpendicular to \( \mathbf{k} = \mathbf{k}/|\mathbf{k}| \) projections. [Hats over vectors refer to unit vectors.] The response function of the bulk solvent is then given in terms of the longitudinal (\( L \)) and transverse (\( T \)) structure factors:

\[
\chi_(\mathbf{k}) = \frac{3 \gamma}{4\pi} \left[ S^L(k) \mathbf{J}^L + S^T(k) \mathbf{J}^T \right] .
\]

Here, \( \mathbf{J}^L = \mathbf{k} \mathbf{k} - \mathbf{J}^T \mathbf{k} \mathbf{k} , \mathbf{J}^T = 1 - \mathbf{J}^L \mathbf{k} \mathbf{k} , \) and \( \gamma = (4\pi/9)\beta m^2 \rho \) is the density of permanent dipoles in a polar solvent, \( m \) is the solute dipole moment, and \( \rho \) is the solvent number density. The structure factors \( S^L, T \) in Eq. (9) are determined by statistics of mutual orientations of solvent dipoles \( \mathbf{m} \). The magnitude \( m \) of the solvent dipole is accounted for by the factor \( \gamma \) in Eq. (9), and the structure factors are given in terms of unit vectors \( \mathbf{\hat{e}}_j = \mathbf{m}_j / m \)

\[
S^L(k) = \frac{3}{N} \sum_{i,j} \left( (\mathbf{\hat{e}}_i \cdot \mathbf{\hat{k}}) (\mathbf{\hat{e}}_j \cdot \mathbf{\hat{k}}) e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \right)_s ,
\]

\[
S^T(k) = \frac{3}{2N} \sum_{i,j} \left( (\mathbf{\hat{e}}_i \cdot \mathbf{\hat{k}}) - (\mathbf{\hat{e}}_j \cdot \mathbf{\hat{k}}) (\mathbf{\hat{e}}_i \cdot \mathbf{\hat{k}}) \right) e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \right)_s ,
\]

where \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \). The value \( k = 0 \) in Eq. (10) gives the continuum limit in which \( S^{L,T}(0) \) is related to the solvent dielectric constant as follows:
\[ S^L(0) = \epsilon - \frac{1}{3y}, \]
\[ S^T(0) = \epsilon - \frac{1}{3y}. \]  

According to the splitting of the response function into two mutually orthogonal \( L \) and \( T \) components, the solvation chemical potential splits into two parts as
\[ \mu_{05} = \mu_{05}^L + \mu_{05}^T, \]  
where each component is determined through the corresponding structure factor
\[ -\mu_{05}^L = \frac{3y}{8\pi} \int \frac{dk}{(2\pi)^2} \left| \tilde{E}_{0}^{L}(k) \right|^2 S^L(k), \]  
\[ -\mu_{05}^T = \frac{3y}{8\pi} \int \frac{dk}{(2\pi)^2} \left| \tilde{E}_{0}^{T}(k) \right|^2 S^T(k). \]  

Here, \( \tilde{E}_{0}^{L}(k) \) and \( \tilde{E}_{0}^{T}(k) \) are the longitudinal and transverse projections of the field \( \tilde{E}_0(k) \).

Unfortunately, the solution given by Eqs. (12) and (13) is applicable only to spherical ions \(^{21}\) when \( \tilde{E}_{0}^{T} = 0 \) and \( \mu_{05}^T \) is identically zero. When either the solute field or/and solute molecular shape are not spherically symmetric, the term \( \mu_{05}^T \) in Eq. (12) leads to “transverse catastrophe.” The transverse structure factor, strongly increasing at small \( k \) values with growing \( \epsilon \), is responsible for the problem.

In the next section, we address this problem for a \( k \)-dependent response function.

**III. SOLVENT RESPONSE FUNCTION**

In order to avoid the transverse catastrophe, alteration of the solvent response by the repulsive core of the solute should be included in the formulation. A general solution for this problem is set up by Chandler’s Gaussian approximation.\(^{24,25}\) This approach is used in the present derivation. The solvent response function can be obtained as the second functional derivative of the generating functional
\[ G(A) = \int e^{iA \cdot \mathbf{P} dr - \beta \mathcal{H}_B} \prod_{r \in \mathcal{B}_0} \delta[\mathbf{P}(r)] d\mathbf{P}. \]

From Eq. (16), the response function \( \chi \) is
\[ \chi(k_1, k_2) = \frac{\beta}{\delta^2 \ln[G(A)]} \frac{\partial^2 A(k_1)}{\partial A(k_2)} \Bigr|_{A=0}, \]
where \( \tilde{A} \) is the Fourier transform of the auxiliary field \( A \). The repulsive core of the solute is taken into account in the functional integral over the polarization field \( \mathbf{P} \) in Eq. (16) by incorporating the product of \( \delta \) functions over the manifold of space points belonging to the solute occupying the volume \( \Omega_0. \)\(^{26}\) The functional integral is weighted with the Gaussian distribution built on the bath Hamiltonian of the pure polar solvent
\[ H_B = \frac{\mathcal{H}_B}{2} \int d\mathbf{k} (\mathbf{P}^{0} \cdot \mathbf{P}) \mathbf{r}^{-1} \mathbf{P}^{*} \cdot \mathbf{P}. \]

After transforming from the direct-space field \( \mathbf{P} \) to the inverted-space field \( \hat{\mathbf{P}} \) and taking Gaussian functional integrals, one arrives at the following expression for the solvent response function:
\[ \chi(k_1, k_2) = \delta(k_1, k_2) \chi_0(k_1) \]
\[ -\chi_0(k_1)[\chi_0(k_1) - \chi_0'(k_1)]^{-1} \theta_0(k_1 - k_2) \chi_0(k_2). \]

The second summand in Eq. (19) is responsible for the alteration of the solvent response function by solute’s repulsive core [cf. Eqs. (7) and (19)]. The kernel \( \theta_0(k_1 - k_2) \) is defined as the Fourier transform of the step function equal to unity inside the solute and zero everywhere else
\[ \theta_0(k) = \int_{\Omega_0} e^{ik \cdot r} dr. \]

The function \( \chi_0' \) entering Eq. (19) is a more complex construction. It is given by the following double integral:
\[ \chi'(k) = \int_{\Omega} d\mathbf{r} \int \frac{d\mathbf{k}'}{(2\pi)^2} \chi_0(k') e^{i(k' - k) \cdot r}. \]

Here, the direct-space integral is taken over the volume \( \Omega' \) outside the body formed by the space points \( r' - \mathbf{r} \) with \( r' \) and \( \mathbf{r} \) belonging to the solute. In the case of a spherical solute considered below, \( \Omega' \) is the space outside a sphere of the radius twice larger than the radius of the closest solute–solute approach \( R_1 = R_0 + \sigma/2 \), where \( \sigma \) is the solvent diameter.

The function \( \chi_0' \) can be recast in terms of two dipole-symmetry projections of the solvent–solute pair distribution function\(^{27}\)
\[ \chi'(k) = \int_{\Omega} d\mathbf{r} e^{i k \cdot r} \left[ \delta(r) + \frac{\rho}{3} \mathcal{H}_{110}(r) - \frac{\rho}{3} \mathcal{H}_{112}(r) \mathbf{D}_r \right]. \]  

where \( \mathbf{D}_r = 3\mathbf{r} \mathbf{r} - 1 \) and \( \mathcal{H}_{110}(r) \) and \( \mathcal{H}_{112}(r) \) are the projections of the solvent pair distribution function on two rotational invariants,\(^{27}\) \( \Delta(12) = (\mathbf{e}_1, \mathbf{e}_2) \) and \( D_{55}(12) = 3(\mathbf{e}_1 \cdot \mathbf{P} \mathbf{e}_2 - (\mathbf{e}_1, \mathbf{e}_2)) \cdot \mathbf{e}_2, \) respectively. The volume \( \Omega' \) is formed by excluding the solvent from the space about twice as large as the volume occupied by the solute. Therefore, for most prac-
tical situations, only the long-range 112 component of the solvent distribution is significant in the direct-space integral in Eq. (22). For a spherical solute, this yields
\[ \chi'(k) = -2A(k)J + A(k)J'. \] (23)
Here, the kernel \( A(k) \) is
\[ A(k) = \frac{4\pi}{3} \int_{\Omega} h^{112}(r)j_z(kr)r^2 dr, \] (24)
where \( j_n(x) \) is a spherical Bessel function.

From Eqs. (9), (19), and (23) the response function can be rewritten in the form
\[ \chi(k_1, k_2) = \delta_{k_1, k_2}\chi_1(k_1) - \chi'(k_1)\theta_0(k_1 - k_2)\chi_1(k_2), \] (25)
where
\[ \chi' = J^L \frac{S^L}{S^L + 2A} + J^T \frac{S^T}{S^T - A}. \] (26)
The kernel \( \theta_0(k_1 - k_2) \) in Eq. (25) leads to the convolution integral over two wave vectors if the response function \( \chi \) is directly used in Eq. (4) to calculate \( \mu_{0\alpha} \). It is more advantageous to avoid inverted-space convolution by transferring the last summand in Eq. (25) back to the direct space when \( \chi(k_1, k_2) \) is integrated with the solute field in Eq. (4). The final result for the solvation chemical potential is then
\[ \mu_{0\alpha} = \mu_{0\alpha}^L + \mu_{0\alpha}^T - \mu_{0\alpha}^{corr}. \] (27)
where the correction term \( \mu_{0\alpha}^{corr} \), arising from the expulsion of the solvent polarization from solute’s volume, is given by the direct-space integral over the solute space \( \Omega \) as follows:
\[ \mu_{0\alpha}^{corr} = -\frac{3y}{8\pi} \int_{\Omega} E_0'(r) \cdot E_0''(r) d\mathbf{r}. \] (28)
The direct-space fields \( E_0' \) and \( E_0'' \) in Eq. (28) are the inverse Fourier transforms of the longitudinal and transverse components of the solute field weighted with structure factors and the A kernel
\[ E_0' = kE_0^L(S^L - S^T) + E_0^T S^T, \] (29)
\[ E_0'' = kE_0^T \left( \frac{S^L}{S^L + 2A} - \frac{S^T}{S^T - A} \right) + E_0^T \frac{S^T}{S^T - A}. \]

Equations (13), (27)–(29) provide a general route to numerical calculations of the solvation chemical potential of a solute of arbitrary shape in dielectric materials. The calculation of the kernel \( A(k) \) and the fields \( E_0' \) and \( E_0'' \) in Eq. (29) is a challenging computational task for solutes of arbitrary shape. The main computational problem arises from the fact that the absolute values of \( \mu_{0\alpha}^L \) and \( \mu_{0\alpha}^{corr} \) are two large numbers at \( \varepsilon \gg 1 \), canceling each other almost identically in Eq. (27). Numerical inaccuracies in the calculation of each of them make direct calculations according to Eqs. (13), (27)–(29) impractical at \( \varepsilon \gg 1.5 \). Exact analytical solutions are very important as benchmarks for numerical algorithms. In the next section, such a solution is given for the case of a point dipole at the center of a spherical solute.

**IV. SPHERICAL DIPOLE SOLUTE**

For a spherical solute with radius \( R_0 \), \( \Omega' \) is the space outside a sphere of the radius \( 2R_1 \). The kernel \( A(k) \) can be found from the asymptotic form for \( h^{112}(r) \) (Ref. 27) applicable at \( r \gg \sigma \), which holds for the integration in Eq. (24) for large solutes with \( 2R_1/\sigma \gg 1 \)
\[ \rho_h^{112}(r) = \frac{(\varepsilon - 1)^2}{4\pi \varepsilon \gamma} \frac{1}{r^3}. \] (30)
The use of Eq. (30) in Eq. (24) yields
\[ A(k) = \frac{(\varepsilon - 1)^2}{3 \varepsilon y} \frac{j_2(2kR_1)}{2kR_1}. \] (31)

The following analysis is based on analytic properties of the response function \( \chi'' \) [Eq. (26)] in the complex \( k \) plane. The analytic properties of the longitudinal \( (\chi'')^L = S^L/(S^L + 2A) \), and transverse \( (\chi'')^T = S^T/(S^T - A) \), components of \( \chi'' \) depend on the analytic properties of \( S^L(k) \), \( S^T(k) \), and \( A(k) \). The function \( A(k) \) as given by Eq. (31) does not have singularities. The thermodynamic stability of the Gaussian Hamiltonian in Eq. (18) requires the response function \( \chi'' \) to be positive and without singularities. Since longitudinal and transverse fluctuations of the solvent polarization can be considered as independent stochastic fields, both \( (S^L)^{-1} \) and \( (S^T)^{-1} \) should be positive and have no singularities. The functions \( (S^L)^{-1} \) and \( (S^T)^{-1} \) may, however, have zeros and these correspond to poles of \( S^L \) and \( S^T \). Such poles in the complex \( k \) plane do appear in Baxter’s analysis of the Percus–Yevick equations for HS fluids and in the corresponding Wertheim’s solution of the MSA equations for dipolar HS fluids.\(^{18}\) What is important is that the poles of \( S^L \) and \( S^T \) cancel out in \( (\chi'')^L \) and \( (\chi'')^T \) [Eq. (26)]. The only source of singularities in the response function \( \chi'' \) are zeros of \( S^L + 2A \) and \( S^T - A \). Zeros of \( S^L + 2A \) are indeed possible at \( \varepsilon \gg 1 \) and large solutes. They are responsible for longitudinal polarization waves generated by the insertion of a solute into a polar solvent. A portion of the free energy of solute stabilization is lost for the generation of these longitudinal waves. This contribution can be exactly determined for dipole solvation and turns out not to exceed about 1% of the solvation free energy (see the Appendix). We therefore will neglect this contribution and assume that the response function \( \chi'' \) is analytic in the complex \( k \) plane. This property leads directly to an analytical solution for the field \( E_0'' \) of a point dipole.

For a point dipole at the center of a spherical cavity, the Fourier transform of the electric field is
\[ \tilde{E}_0(k) = -4\pi j_1(kR_1) \frac{kR_1}{kR_1} [3\tilde{k} \cdot \mathbf{m}_0 - \mathbf{m}_0]. \] (32)
When Eq. (32) is substituted into Eq. (29), the field \( \Delta E_0'' \) can be obtained by contour integration in the complex \( k \) plane. Since \( \chi'' \) is analytic, the only contribution to the integral at \( r < R_1 \) is the \( k = 0 \) pole of \( \tilde{E}_0 \). This yields (see the Appendix)
\[ E_0'' = \frac{2(S^T(0) - S^T(0))}{3gkR_1^2}. \] (33)
\[ g_K = S^L(0) + 2A(0) = S^T(0) - A(0) \]
\[ \text{as follows:} \]

is the Kirkwood factor of the polar solvent. Note that numerical calculations of the field \( E'_\nu \) are in a very good agreement with Eq. (33), further indicating that the poles at \( S^L + 2A = 0 \) do not produce any significant contribution to \( E'_\nu \). With Eq. (33) substituted into Eq. (28), the correction term in the chemical solvation potential becomes

\[ \mu_{0s} = -\frac{2(S^T(0) - S^L(0))}{3g_K R_1^3} m_0 \int_0^\infty \frac{dF_0}{2\pi^2} \theta_0(\hat{E}S^T_0(S^L - S^T) } + E_0S^T \] (35)

Noting that for a spherical solute

\[ \theta_0(k) = 4\pi R_1^2 j_k(kR_1) kR_1 \] (36)

one gets for the correction term

\[ \mu_{0s} = \frac{S^T(0) - S^L(0)}{3g_K} (2\mu_{0s}^L - \mu_{0s}^T) \] (37)

The final expression for the solvation chemical potential follows from Eqs. (27) and (37)

\[ \mu_{0s} = \frac{S^T(0)}{g_K} \mu_{0s}^L + \frac{S^L(0)}{g_K} \mu_{0s}^T \] (38)

Equation (38) can be rewritten taking account of Eq. (11), connecting the \( k=0 \) structure factors to the dielectric constant, as follows:

\[ \mu_{0s} = \frac{3}{2\epsilon + 1} [\epsilon \mu_{0s}^L + \mu_{0s}^T] \] (39)

The Onsager equation [Eq. (1)] with \( a = R_1 \) can be obtained from Eq. (39) when \( S^L(k) = S^L(0) \) and \( S^T(k) = S^T(0) \) are used for the calculation of \( \mu_{0s}^{L,T} \) in Eq. (13). So-obtained continuum values for a point dipole are \( \mu_{0s}^L = -2m_0^2(\epsilon - 1)/9\epsilon R_1^3 \) and \( \mu_{0s}^T = -m_0^2(\epsilon - 1)/9\epsilon R_1^3 \), which yields the Onsager equation when substituted into Eq. (39).

For Stokes shift measurements, it is important to know the solvation chemical potential due to nuclear solvent polarization only. In this case, the polarization structure factors should describe orientational correlations of the permanent dipoles. The \( k=0 \) values are then given by the following relations:

\[ S^L(0) = c_0/3 \] (40)
\[ S^T(0) = (\epsilon - \epsilon_\infty)/3\epsilon_\infty \] (40)

where \( \epsilon_\infty \) is the high-frequency dielectric constant and \( c_0 = \epsilon_\infty - 1 \) is the Pekar factor. With these values for the \( k=0 \) structure factors, Eq. (38) transforms to

\[ \mu_{0s} = \frac{3}{2\epsilon + 1} [\epsilon \mu_{0s}^L + \mu_{0s}^T] \] (41)

Note that the chemical potential components \( \mu_{0s}^{L,T} \) in Eq. (41) are defined as integrals with the structure factors describing nuclear polarization fluctuations.

V. DISCUSSION

Equations (38) and (39) are the central results of this study. They indicate that the longitudinal \((L)\) and transverse \((T)\) components of the solvation chemical potential appearing in direct perturbation expansions [Eq. (12)] also enter the exact solution. The change in the solvent response function caused by the expulsion of the dipolar polarization from the solute volume leads to the appearance of the factors \( 3\epsilon/(2\epsilon + 1) \) and \( 3/(2\epsilon + 1) \) in front of \( L \) and \( T \) components, respectively [cf. Eqs. (12) and (39)]. The renormalization of the transverse response is particularly important as it eliminates the transverse catastrophe of the direct perturbation expansions. Equation (39) actually indicates that transverse response becomes increasingly insignificant with increasing solvent dipolar strength, and solvation in strongly polar solvents is dominated by the longitudinal dipolar polarization. This result is in qualitative agreement with solvation dynamics simulations showing that longitudinal dielectric dynamics make the main contribution to the Stokes shift correlation function of dipolar chromophores.

Equation (39) gives an exact solution for the LRA solvation chemical potential in a dielectric with an arbitrary dispersion of polarization fluctuations given by the longitudinal and transverse polarization structure factors. The derivation does not assume any particular physical mechanisms of polarization fluctuations and is limited only by the assumption of their Gaussian statistics. Therefore, polarization structure factors from experiment, simulations, or liquid-state theories can be used in Eq. (39). This approach is realized in our calculations below where structure factors of model multipolar fluids obtained from MC simulations are used in Eq. (39) to calculate the solvation chemical potential.

In the case of polar solvents composed of molecules of arbitrary shape and charge distribution, dipolar projections can be extended to solvation structure factors, more general charge−charge structure factors can be used for the longitudinal and transverse structure factors. With the frequency-dependent structure factors \( S^L(k, \omega) \) and \( S^T(k, \omega) \) Eqs. (38) and (39) can be extended to solvation dynamics. In this respect, the solution provides an exact route between solvent properties and solvation characteristics which can be used as a reliable tool for probing properties of complex condensed media.

Of course, optical dyes are not point dipoles. The solution, however, may appear to be useful for a broader range of situations than it strictly applies to. The only place where the point dipole symmetry of the solute field has been used is the calculation of the field \( E'_\nu \). The components \( \mu_{0s}^L \) and \( \mu_{0s}^T \) depend on corresponding \( L \) and \( T \) projections of the solute field. The latter can be calculated numerically as Fourier transform of the electric field produced by a fairly general charge distribution within an overall neutral molecule. The same applies to the molecular shape. The solute can be specified by a set of fused spheres representing atoms or molecular groups with numerical Fourier transform producing the
The ratio of the solute and solvent dipoles, $m_0/m = 4.0$, was held constant when $m$ was changed since under this condition the LRA holds most accurately. The accuracy of the LRA was checked on the condition that the absolute value of the average solute–solvent interaction energy, $\langle v_{0s} \rangle$, is equal to the second cumulant divided by $k_B T$. This condition holds within 5% in all simulations. The necessity to maintain the LRA is responsible for the use of simulations with nonzero solute dipole instead of equilibrium configurations around a nonpolar solute as in Eq. (2). In the latter case the polarity dependence of the solvation thermodynamics becomes affected by partial dewetting of solute’s surface leading to the breakdown of the LRA. Keeping a constant ratio of solute vs solvent dipole moment while increasing $y$ prevents this from happening. The details of the simulation procedure are given elsewhere.

Figure 2 presents the comparison of the calculations according to Eqs. (13) and (39), with the polarization structure factors obtained from MC simulations, to solvation simulation results for purely dipolar (circles) and dipolar–quadrupolar (squares) solvents. The dashed lines refer to the Onsager equation at $a = R_0$ (upper curves) and $a = R_0 + \sigma/2$ (lower curves). The results of the calculations are sensitive to the presence of quadrupoles affecting the strength of dipole–dipole correlations in the solvent. The change in dipole–dipole correlations in turn affects polarization structure factors and with that the calculated values of $\mu_{0s}$ and $\mu_{0q}$. The continuum equation is almost insensitive to the presence of quadrupoles in polar solvents since it predicts saturation of the solvent response at $\epsilon \gg 1$.

The simulated values of the solvation chemical potential fall above the results of calculations according to Eq. (39). This outcome is not unexpected. The present formalism takes into account the alteration of the solvent polarization response by the repulsive core of the solute, but does not incorporate the corresponding alteration in the solute–solvent density profile represented by the spherically symmetric solute–solvent pair correlation function $h_{0s}(r)$. The corresponding contribution to $\mu_{0s}$ makes solute’s stabilization energy more negative (density reorganization energy). Since only approximate schemes to calculate this component are currently available, we do not address this issue here.

Figure 3 shows the longitudinal, $3\mu_{0s}^L/(2 + 1)$ (squares), and transverse, $3\mu_{0s}^T/(2 + 1)$ (diamonds), components of $\mu_{0s}$ at various $y$ calculated from Eqs. (13) and (39). The filled points refer to the calculations with the full solute field in Eq. (5). It remains to be tested on computer simulations how accurate this approach may be in application to common dipolar dyes.

The results of calculations according to Eq. (39) are compared here to MC simulations of dipole solvation in dipolar and dipolar–quadrupolar HS solvents. Two types of simulations have been carried out. Simulations of pure liquids of varying dipole moment were performed to produce the polarization structure factors necessary for the calculation of $\mu_{0s}$ and $\mu_{0q}$ [Eq. (13)]. Standard Metropolis algorithm with reaction field correction for the cutoff of multipolar forces was used for 500 and 864 solvent molecules in a cubic simulation box. The length of simulation runs was varied depending on solvent polarity between $8 \times 10^5$ and $1.2 \times 10^6$ MC cycles. Neumann’s formalism for accounting for the reaction field cutoff of dipole–dipole forces in the calculation of the structure factors was employed. Pure HS dipolar liquids with dipole moment $m$ and HS dipolar liquids with dipole moment and axial quadrupole $Q$ were simulated at changing $m$ and $\rho a^3 = 0.8$. For dipolar–quadrupolar solvents, the axial quadrupole moment was fixed at the reduced value of the average solute–solvent interaction energy more negative $10$, $\rho a^3 = 0.8$. The dashed and dash-dotted lines indicate the Onsager result [Eq. (11)] at $Q = 0$ and $(Q^*)^2 = 0.5$, respectively. The Onsager curves were obtained by using $\epsilon$ from simulations with $a = R_0$ (upper curves) and $a = R_1$ (lower curves). The solute radius relative to the solvent diameter is $R_0/\sigma = 0.9$, $\rho a^3 = 0.8$. This condition holds within 5% in all simulations. The necessity to maintain the LRA is responsible for the use of simulations with nonzero solute dipole instead of equilibrium configurations around a nonpolar solute as in Eq. (2). In the latter case the polarity dependence of the solvation thermodynamics becomes affected by partial dewetting of solute’s surface leading to the breakdown of the LRA. Keeping a constant ratio of solute vs solvent dipole moment while increasing $y$ prevents this from happening. The details of the simulation procedure are given elsewhere.

In the second set of simulations, spherical dipolar solutes of the radius $R_g/\sigma = 0.9$ were immersed in the solvent, and the second cumulant of the solute–solvent dipole–dipole interaction potential was measured on simulated solvent configuration. The length of simulations was varied between $1.0 \times 10^5$ and $1.5 \times 10^6$ MC cycles. The solvent properties were taken the same as for simulations of pure solvents. We stress here that the full dipole–quadrupole potential was used in MC simulations, and only its dipole–dipole solute–solvent component was used to analyze the simulation data in order to study the solvation thermodynamics of dipolar solvent polarization.
$S^{L-T}(k)$ structure factors, and the open points indicate the continuum-limit calculations with $S^{L-T}(0)$ in Eq. (13). The longitudinal component of $\mu_{0s}$ prevails in strongly polar solvents since the transverse contribution scales with the factor $3/(2\varepsilon+1)$. Note, however, that the continuum limit keeps both contributions at the comparable magnitude for all solvent polarities. This is easy to see from rescaling the two summands in Eq. (14) with the $3\varepsilon/(2\varepsilon+1)$ and $3/(2\varepsilon+1)$ factors from Eq. (39). Therefore, the disappearance of the transverse contribution to the solvation chemical potential [cf. filled and open diamonds in Fig. 3] is a result of the microscopic nature of the solvent response leading to a sharp decay of $S^{T}(k)$ at $kr<\pi$ in strongly polar solvents.\(^{10}\) The latter circumstance limits the applicability of the continuum assumption $S^{T}(k)=S^{T}(0)$ to a range of low polarities which depends on the relative dimensions of the solute and the solvent.

The most striking peculiarity seen in Fig. 3 is a very significant distinction between continuum and microscopic calculations of the longitudinal component of $\mu_{0s}$. The nonlocal, $k$-dependent part of the solvent response function thus makes a significant contribution to the solvation thermodynamics. Any continuum calculation using $S^{L-T}(0)$ neglects this component of the response (cf. the filled and open squares in Fig. 3). This deficiency is commonly compensated by choosing the cavity radius smaller than the distance of the closest solute–solvent approach, $R_0+\alpha/2$. However, the portion of $S^{L-T}(k)$ contributing to the $k$ integral in Eq. (13) is affected by both the solute size and solvent polarity. Consequently, the cavity radius depends on the solvent as well as the solute/solvent size ratio. These reasons are fundamentally responsible for the fact that various schemes to define dielectric cavities for continuum calculations have failed to provide an algorithm generally applicable to a wide variety of solvents and solute geometries.

Noteworthy is a linear trend of the longitudinal component $\mu_{0s}^{L}$, and the total solvation chemical potential, with the polarity parameter $y$ at large $y$ values. This peculiarity was first observed in MC simulations\(^{10}\) and is qualitatively different from saturation of $\mu_{0s}$ with $y$ predicted by continuum models (cf. the filled and open squares in Fig. 3). A linear dependence of $\mu_{0s}$ on $y$ seems to be a general rule for multipolar solvation in strongly polar solvent within the LRA.\(^{31}\) This linear trend breaks down with saturation of the solvent response due to nonlinear solvation predominantly caused by partial dewetting of solute’s surface in highly polar solvents.\(^{10}\)

The present formulation relies on the LRA to connect the second cumulant of the solute–solvent interaction energy to the solvation chemical potential. The second cumulant is, however, a useful property on its own in cases when the LRA breaks down, e.g., at supercritical densities. In such cases, $(\langle \delta v_{0s} \rangle^2)_0$ is the dipolar polarization contribution to the spectral width of optical transition from a nondipolar to a dipolar state.

**ACKNOWLEDGMENT**

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS (39539-AC6) for support of this research.

**APPENDIX: DERIVATION OF FIELD $E_0^\alpha$**

From Eqs. (29) and (32), the direct-space field $E_0^\alpha(r)$ is given by the following relation:

$$E_0^\alpha(r) = -\frac{m_0}{\pi R_1} \int_{-\infty}^{\infty} dk j_0(kR_1) \left\{ \frac{2S^L}{S^L+2A} + \frac{S^T}{S^T-A} \right\}$$

$$\times \left[ \frac{1}{3} j_0(kr) - \frac{D_r}{3} j_2(kr) \right] - \frac{S^T}{S^T-A} j_0(kr). \tag{A1}$$

The $k$ integral can be calculated as a contour integral with the integration contour closed in the upper-half complex $k$ plane. Since $r<R_1$ in the space integral in Eq. (28), one needs to consider the $k=0$ pole of $j_1(kR_1)$ and the poles arising from $S^L(k)+2A(k)=0$. At $k=0$ $j_2(kr)\approx k^2$ and the terms containing $j_2(kr)$ give zero contribution to the $k=0$ pole. The final equation for $E_0^\alpha(r)$ then becomes

$$E_0^\alpha(r) = \frac{2m_0}{3\varepsilon kR_1^\alpha} \left( S^T(0) - S^L(0) \right) - \sum_j \frac{2S^L(k_j^\alpha)}{3\varepsilon k_j^\alpha R_1^\alpha}$$

$$\times e^{iks_j^\alpha R_1^\alpha} \left( 1 - ik_j^\alpha R_1^\alpha \right) \left[ m_0(j_0(k_j^\alpha r) - j_2(k_j^\alpha r)) \right]. \tag{A2}$$

where $s_j^\alpha = d(S^L+2A)/dk_j^\alpha$ and $k_j^\alpha$ are the roots of the equation $S^T(k_j^\alpha)+2A(k_j^\alpha)=0$, such that $\text{Im}(k_j^\alpha)>0$. Equation (33) follows from Eq. (A2) by neglecting the second summand arising from the poles of $S^T/(S^L+2A)$. Real solutions $\text{Im}(k_j^\alpha)=0$ give the largest contribution to $E_0^\alpha$. When expression (A2) with these roots is used in Eq. (28) the contribution from singularities $k_j^\alpha$ does not exceed 1% of the value of $\mu_{0s}^{\text{corr}}$.

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