

Nonlocal continuum solvation model with oscillating susceptibility kernels: A nonrigid cavity model

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(Received 13 October 1997; accepted 9 February 1998)

A nonlocal continuum theory of solvation is applied using an oscillating dielectric function with spatial dispersion. It is found that a convergent solution cannot be calculated using a model of a fixed solute cavity inside the solvent continuum. This is attributed to the fact that the dielectric oscillations appear as a result of coupling between polarization and density fluctuations, contradicting the concept of a fixed cavity. The theory is corrected by allowing the cavity size to vary. A cavitation energy and an interaction between the medium reaction field and the cavity size are added to the solvation free energy, and a new theory obtained by a variational treatment. The interaction term enables convergent solutions to become attainable, resulting in an oscillating electrostatic solvation energy as a function of cavity radius, the cavitation term enables these oscillations to be smoothed out, resulting in a regular, monotonic solvation free energy. © 1998 American Institute of Physics. [S0021-9606(98)50319-4]

I. INTRODUCTION

In our preceding paper¹ we elaborated a new algorithm for solving the nonlocal Poisson equation in nonuniform electrostatic systems modeling solvation phenomena. According to this model the solute charge density is surrounded by a cavity in which no polarization effects occur, whereas the external volume is described in terms of the equations of nonlocal electrostatics. In operator notation the dielectric permittivity operator $\hat{\epsilon}$ and susceptibility operator $\hat{\chi}$ are defined as

$$\begin{aligned}\hat{\epsilon} &= \epsilon_{\infty} + 4\pi\hat{\chi}, \\ \epsilon_{\infty} &= 1 + 4\pi\chi_{\infty},\end{aligned}\quad (1.1)$$

$$\hat{\chi}F(\mathbf{r}) = \int d^3\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}')F(\mathbf{r}'),$$

where $F(\mathbf{r})$ is a smooth function and ϵ_{∞} and χ_{∞} denote the high-frequency dielectric permittivity and polarizability respectively. Note that in general the dielectric operator is a tensor. However, as mentioned in the preceding paper, the transverse component of the tensor is eliminated within Maxwell's equations. Therefore in this paper wherever we refer to a dielectric (scalar) function, ϵ or χ , we specifically have in mind the longitudinal component. The susceptibility kernel is then described as a step function on the boundary surface S of the cavity:

$$\chi(\mathbf{r}, \mathbf{r}') = \begin{cases} \chi(|\mathbf{r}-\mathbf{r}'|) & \text{both } \mathbf{r} \text{ and } \mathbf{r}' \in V_e \\ 0 & \text{one or both of } \mathbf{r}, \mathbf{r}' \in V_i \end{cases}, \quad (1.2)$$

where V_i and V_e are the internal and external volumes divided by S . This model, accounting for matching conditions on the boundary surface S , can be solved analytically for smooth Lorentzian models of the dielectric function $\chi(k)$,

the Fourier transform of kernel $\chi(|\mathbf{r}-\mathbf{r}'|)$ in Eq. (1.2). Such a solution had been found previously,^{2,3} although approximate treatments of this model are more familiar.⁴⁻⁷ Recent studies of microscopic molecular solvent models⁸⁻¹⁶ have brought into doubt the validity of the Lorentzian solvent model, claiming that $\chi(k)$ has a pole structure leading to oscillatory behavior in the corresponding polarizability kernels $\chi(|\mathbf{r}-\mathbf{r}'|)$. We shall investigate here the consequences of this type of behavior.

As our calculations show, the most striking result of the pole model, as applied to solvation effects for spherical ions, is an irregular behavior in the solvation energy U_s as a function of ion radius a . The possibility of irregular behavior in $U_s(a)$ was briefly touched upon in an earlier work¹⁷ where a different pole model was used. The excluded volume effect was inconsistently treated in this study, which created an artificial dependence of U_s on the spherical solute charge distribution inside the cavity. By empirically varying the charge distributions inside ions, it was possible to smear away irregularities in the function $U_s(a)$.^{8,17} The present exact cavity model does not allow for this possibility. The struggle with these irregularities thus necessitates the invocation of advanced cavity models introduced by the so-called regularization procedures^{18,19} for solving the main integral equation of the theory, and by considering variations in the cavity radius.²⁰⁻²³

As a result, we suggest a consistent nonlocal continuum model of solvation based on a variational approach, formulated here for a spherically symmetric solute. The corresponding free energy functional (FEF) includes as variables both the polarization field and the cavity radius on equal grounds. The regularization procedure is naturally introduced in the variational equations via the interaction of the variables. Smooth solvation energy curves are obtained by this technique.

The experience gained by studying these advanced mod-

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els draws us to the following conclusions. The addition of pole terms to a Lorentzian function for $\chi(k)$ violates the positive definiteness of the integral operator governing the basic equation of the theory with an excluded volume.⁶ This is the fundamental origin of the instability in the equation's solution. Modifications of the cavity model are aimed at re-generating the correct properties of the the integral kernel or, at the very least, serve to approach them as close as possible. At a physical level of reasoning we observe that oscillations introduced by poles in $\chi(k)$, related to spatial correlations inside a solvent, are incompatible with the frozen solute cavity model, in which the cavity radius a is considered as an intrinsic property of a given solute ion. The modifications here of the cavity model introduce more flexibility by allowing for the mutual adjustment of the cavity size and solvent structure in the close vicinity of the ion. Altogether we completely or almost completely return to a theory with a positive-definite kernel in which no instabilities arise.

For practical applications this notion suggests that simple Lorentzian models of $\chi(k)$, postulating the complete annihilation of the above-mentioned sophisticated effects and thus having no instability problems, seem to have a reasonable justification and may serve as a background for a semiempirical nonlocal continuum solvation theory.

II. THE SPHERICAL CAVITY MODEL

Let us consider the spherically symmetric case as introduced in Ref. 1. The electrostatic potential is expressed as

$$\Psi(R) = \varphi(R) + \xi(R) + \Phi(R), \quad (2.1)$$

where

$$\varphi(R) = Q/R,$$

$$\xi(R) = \begin{cases} 4\pi \int_a^\infty dR' g(R') R' & (R \leq a) \\ 2\pi \int_a^\infty dR' g(R') (R + R' - |R - R'|) \frac{R'}{R} & (R > a) \end{cases}, \quad (2.2)$$

$$\Phi(R) = \begin{cases} 4\pi a\sigma & (R \leq a) \\ 4\pi a^2\sigma/R & (R > a) \end{cases}.$$

The vacuum potential $\varphi(R)$ is created by a point charge Q located at the center of the cavity. The cavity radius is denoted by a . The medium potential is a sum of two terms. The first, $\xi(R)$, appears due to the external charge distribution $g(R)$, induced by polarization of the external volume. The second, $\Phi(R)$, represents the potential created by surface charge density σ . We are using spherical coordinates here:

$$\mathbf{r} \rightarrow (R, \theta, \phi); \quad \mathbf{r}' \rightarrow (R', \theta', \phi'). \quad (2.3)$$

The following basic equations define $g(R)$ and σ :¹

$$g(R) + \frac{4\pi}{\epsilon_\infty} \int_a^\infty dR' \gamma(R, R') g(R') = -\frac{1}{\epsilon_\infty} \left(\frac{Q}{a^2} + 4\pi\sigma \right) \gamma(R, a), \quad (2.4)$$

$$\sigma = \sigma_\infty + \frac{1}{\epsilon_\infty} \int_a^\infty \beta(a, R') \frac{\partial \Psi}{\partial R'} dR',$$

where

$$\sigma_\infty = -\frac{Q}{4\pi a^2} \left(1 - \frac{1}{\epsilon_\infty} \right). \quad (2.5)$$

The one-dimensional nonlocal kernels appear as a result of averaging the kernel $\chi(|\mathbf{r}-\mathbf{r}'|)$ over angular variables:

$$\gamma(R, R') = R'^2 \int d\phi' \sin\theta' d\theta' \chi(|\mathbf{r}-\mathbf{r}'|), \quad (2.6)$$

$$\beta(R, R') = \frac{R'^2}{\cos\theta} \int d\phi' \sin\theta' \cos\theta' d\theta' \chi(|\mathbf{r}-\mathbf{r}'|).$$

Spherical symmetry allows calculations here to be performed with $\theta = \phi = 0$.¹

The equilibrium solvation energy is given by the expression

$$U_s = \frac{1}{2} \int_{V_i} d^3\mathbf{r} \rho(\mathbf{r}) (\xi(\mathbf{r}) + \Phi(\mathbf{r})) = 2\pi Q \left[a\sigma + \int_a^\infty dR R g(R) \right]. \quad (2.7)$$

III. NUMERICAL EXPERIMENTS WITH OSCILLATING SUSCEPTIBILITY FUNCTIONS

We now expand the nonlocal approach by introducing oscillating components into the susceptibility operator. For the Fourier transformed kernel $\chi(k)$ this means that pole terms are added to the Lorentzian terms, generating an oscillating kernel modulated by a decaying exponential in real space. Such poles have been found in recent microscopic molecular structural studies of polar liquids.⁸⁻¹⁶ In terms of the definition suggested by Eqs. (1.1), (1.2) we have

$$\chi(|\mathbf{r}-\mathbf{r}'|) = \left(\frac{1}{2\pi} \right)^3 \int d^3k e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \chi(k) \quad (3.1)$$

$$= \frac{1}{2\pi^2} \int_0^\infty dk k^2 \frac{\sin(k|\mathbf{r}-\mathbf{r}'|)}{k|\mathbf{r}-\mathbf{r}'|} \chi(k), \quad (3.2)$$

where

$$\chi(k) = \frac{\chi_L}{1 + \lambda^2 k^2} + \frac{\chi_{p1}}{1 - (k/k_1)^2} - \frac{\chi_{p2}}{1 - (k/k_2)^2}, \quad (3.3)$$

$$\chi_L, \chi_{p1}, \chi_{p2} > 0, \quad k_2 > k_1.$$

The form of the pole components given here with positive signs for constants $\chi_L, \chi_{p1}, \chi_{p2}$ is determined by stability

properties of the dielectric permittivity function.^{8,9,24} Additionally the following normalization condition must be satisfied:

$$\begin{aligned}\chi(k=0) &= \chi_0 - \chi_\infty, \\ \chi_0 &= \frac{1}{4\pi}(\varepsilon_0 - 1), \\ \chi_\infty &= \frac{1}{4\pi}(\varepsilon_\infty - 1),\end{aligned}\quad (3.4)$$

where χ_0 and χ_∞ are the static and optical polarizability constants. General stability criteria imply that²⁴

$$\chi(k) > 0 \quad \text{or} \quad \chi(k) < -1/4\pi. \quad (3.5)$$

By direct integration the following expressions are obtained for the integral kernels $\gamma(R, R')$ and $\beta(R, R')$, defined in Eqs. (2.6):

$$\begin{aligned}\gamma(R, R') &= \gamma_L(R, R') + \gamma_{p1}(R, R') + \gamma_{p2}(R, R'), \\ \beta(R, R') &= \beta_L(R, R') + \beta_{p1}(R, R') + \beta_{p2}(R, R'),\end{aligned}\quad (3.6)$$

where $\gamma_L(R, R')$ and $\beta_L(R, R')$ are given by¹

$$\begin{aligned}\gamma_L(R, R') &= -\frac{\chi_L}{2\lambda} \frac{R'}{R} (\exp(-(R+R')/\lambda) \\ &\quad - \exp(-|R-R'|/\lambda)),\end{aligned}\quad (3.7)$$

$$\begin{aligned}\beta_L(R, R') &= \frac{\chi_L}{2\lambda R^2} (e^{-(R+R')/\lambda} (\lambda+R)(\lambda+R') \\ &\quad - e^{-|R-R'|/\lambda} (\lambda^2 + \lambda|R-R'| - RR')), \end{aligned}$$

and the pole contributions are

$$\begin{aligned}\gamma_{pi}(R, R') &= -\frac{\chi_{pi} k_i}{2} \frac{R'}{R} [\sin(k_i(R+R')) \\ &\quad - \sin(k_i|R-R'|)],\end{aligned}\quad (3.8)$$

$$\begin{aligned}\beta_{pi}(R, R') &= \frac{\chi_{pi}}{R^2 k_i} (k_i R \cos k_i R - \sin k_i R) \\ &\quad \times (\cos k_i R' + k_i R' \sin k_i R')\end{aligned}$$

for $i=1,2$. Note that the functions β_{pi} apply only for $R < R'$, since we in fact only require $\beta_{pi}(a, R')$, i.e. $R = a < R'$. The case $R > R'$ is omitted for the sake of brevity.

With these underlying relations we solve the basic equations (2.4) and describe the new phenomena observed when kernels of the form (3.6)–(3.8) are studied. Contrary to the analytical treatment of Ref. 1, we must invoke a numerical procedure⁶ for solving the integral equation for $g(R)$ (first equation in (2.4)).

Using parameters for $\chi(k)$ as described in Sec. V (see Eq. (5.2)), we were able to find regular solutions for selected values of the cavity radius a . These solutions represent the induced charge distributions $g(R)$, surface charge densities σ and solvation energies U_s which, for an appropriate parametrization, seem to have attained reasonable values. A new qualitative result was the oscillating nature of the function $g(R)$ (see Fig. 1 for an example under slightly modified

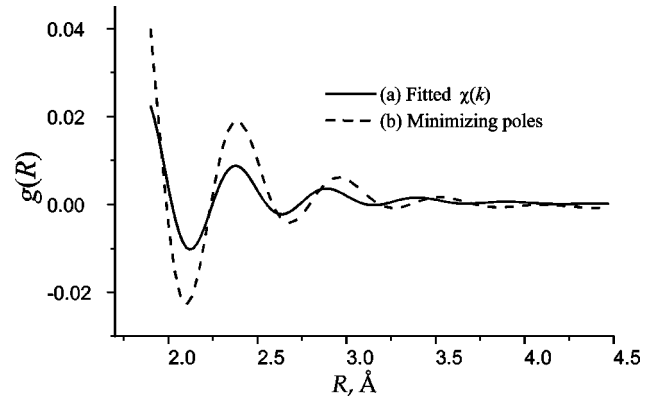


FIG. 1. Sample result for induced charge distribution $g(R)$ (10^9 V m^{-1}) for a nonlocal electrostatic model of water with a fixed cavity, using Bakushinsky regularization. (a) Parameters fitted to published dielectric function Ref. 9, see Eq. (5.2), $\alpha=5$. (b) Parameters minimizing poles, see Eq. (5.3), $\alpha=1$. Cavity radius $a=1.9 \text{ \AA}$. Ion charge $=-1 \text{ a.u.}$

conditions), compatible with intuitive expectations based on the experience of molecular calculations.

It is only as we shift the radius a that we encounter a problem with instability. Although for a given value of σ we can always obtain a unique solution to the first equation in (2.4) for $g(R)$ (this is assured by the stable matrix numerical procedure⁶), the whole iterative process for both equations (2.4) fails to converge. This instability manifests itself at regular intervals (for increasing a); the intervals appear to be related to the poles in $\chi(k)$, since the regions of nonconvergence are separated by approximately π/k_2 .

IV. THE REGULARIZATION PROCEDURE

The instabilities observed in the preceding section can be understood in terms of the theory of integral equations.^{18,25} The first equation in (2.4) is a Fredholm integral equation of the second kind. It can be written in an operator form:

$$(I + 4\pi\hat{\Gamma})g(R) = f(R), \quad (4.1)$$

$$f(R) = -\frac{1}{\varepsilon_\infty} \left(\frac{Q}{a^2} + 4\pi\sigma \right) \gamma(R, a).$$

The integral operator is defined by the relation

$$\hat{\Gamma}F(R) = \int_a^\infty \gamma(R, R')F(R')dR', \quad (4.2)$$

where $F(R)$ is an arbitrary function. Equation (4.1) has a unique solution provided the operator

$$\hat{A} = I + 4\pi\hat{\Gamma} \quad (4.3)$$

has no zero eigenvalues. If such an eigenvalue actually exists and corresponds to the eigenfunction $g_0(R)$:

$$(I + 4\pi\hat{\Gamma})g_0(R) = 0, \quad (4.4)$$

then Eq. (4.1) becomes inconsistent unless its right-hand side is orthogonal to $g_0(R)$:

$$(g_0(R), f(R)) = 0, \quad (4.5)$$

where (\dots, \dots) indicates a scalar product. These complications are completely eliminated only when operator \hat{A} (4.3) is positive-definite, as is the case for a pure Lorentzian model. In this case the kernels $\gamma(R, R')$ and $\beta(R, R')$ are exponentially decaying functions (see Eq. (3.7)).

For the cases (3.6)–(3.8), contrary to the Lorentzian model, both positive and negative eigenvalues in \hat{A} are expected. In general the operator \hat{A} has a continuous spectrum of eigenvalues, therefore a zero eigenvalue is expected to exist. Our numerical procedure works with a matrix representation of \hat{A} .⁶ Thus, for a given cavity radius a , the appearance of the exact zero eigenvalue is unlikely. However, because a is a continuous parameter, a singularity in the solution cannot be avoided. This phenomenon underlies the numerical problems described above.

Such a phenomenon is known in computational mathematics¹⁸ as a statement that discrete numerical procedures become unstable and diverge in the vicinity of a singular point where the above-stated Fredholm consistency conditions are violated. The corresponding breakdown of the straightforward nonlocal theory seems to indicate that the concept of a frozen cavity (with a fixed radius a) is physically incompatible with non-positive-definite susceptibility kernels. For such kernels we need to introduce a modification into the original integral equation [the first equation in (2.4)], eliminating its singularities. This is known as a ‘regularization procedure’¹⁸ and in Sec. VII will be incorporated explicitly into the nonlocal theory in the context of a nonrigid cavity model. At this point we merely demonstrate its effectiveness in removing divergencies in the solution to Eq. (2.4).

A simple way to regularize a matrix representation of operator \hat{A} (4.3) is to exclude its near-zero eigenvalues, complemented by a simultaneous elimination of the corresponding eigenvector components in function $f(R)$, see Eq. (4.5). This is achieved by applying the Bakushinsky method.^{18,19} Here a small imaginary term is added to the singular operator \hat{A} , and Eq. (4.1) becomes

$$(\hat{A} + i\alpha I)g_\alpha = f, \quad (4.6)$$

where α is a small quantity and I is the identity operator. Multiplying on the left by $\hat{A} - i\alpha I$, and taking the real part only (which converges to the desired solution in the limit $\alpha \rightarrow 0$), we find that the solution to this equation can be represented as

$$g_\alpha(R) = (\alpha^2 I + \hat{A}^2)^{-1} \hat{A} f(R). \quad (4.7)$$

Singularities in \hat{A} are obviously eliminated in this expression. Moreover, singular components [violating Eq. (4.5)] are projected away by the product $\hat{A}f(R)$ on the right-hand side of Eq. (4.7).

Ideally, one must consider the limit of Eq. (4.7) with $\alpha \rightarrow 0$. In practice only finite values of α can provide satisfactory results. Since α renormalizes the operator $I + 4\pi\hat{\Gamma}$ [Eqs. (4.3) and (4.6)], which in turn is related to the operator $\hat{\epsilon}$ (this is actually a projection of the operator $\hat{\epsilon}$ on the external volume²), we can judge the condition $\alpha \rightarrow 0$ by comparing α

with ϵ_0 . A proper α value together with the Bakushinsky solution Eq. (4.7) is considered as a necessary empirical ingredient of the extended concept of a frozen cavity in solvation theory. In the theory with a nonrigid cavity (Secs. VI–VIII), α may be considered as a parameter of the theory which measures the strength of the interaction between the electric field of the medium and cavity variables.

V. ILLUSTRATIVE CALCULATIONS

The model of the susceptibility function suggested by Eq. (3.3) is supported by recent MD simulations of water,⁹ in which a minimum was found in $\chi(k)$ in the region between $k=0$ and the first pole. Therefore as a first step we take the solvent here to be water, for which the pole parameters are given by⁹

$$k_1 = 1.0 \text{ \AA}^{-1}; \quad k_2 = 12.5 \text{ \AA}^{-1}. \quad (5.1)$$

In order to define the parameters for the function $\chi(k)$, Eq. (3.3), we adjusted the parameters λ and $\chi_1 = \chi_2$ so as to best reproduce the functions $\epsilon(k) = 1 + 4\pi\chi(k)$ and $f(k) = 1 - 1/\epsilon(k)$, presented for water in Ref. 9. More precisely, we attempted to fit the low k minimum in $\epsilon(k)$, $\epsilon(0.6) \approx 17$ (that is, $\chi(0.6) \approx 1.3$), and the maximum in $f(k)$, $f(3) \approx 25$. We must note here that the quantities in Ref. 9 were made with $\epsilon(\infty) = 1$; we, on the other hand, have assumed $\epsilon(\infty) = \epsilon_\infty = 1.7756$. It should also be noted that we have assumed that the stability conditions (3.5) must be obeyed by the susceptibility function $\chi(k)$, and therefore special care has been taken to ensure they are satisfied. The final set of parameters which we employed for water ($\epsilon_0 = 78.39$) is

$$\begin{aligned} \lambda &= 2.95 \text{ \AA}, & k_1 &= 1.0 \text{ \AA}^{-1}, & k_2 &= 12.5 \text{ \AA}^{-1}, \\ \chi_L &= 6.096, & \chi_1 &= \chi_2 = 0.209, \\ \chi_0 &= 6.158, & \chi_\infty &= 0.0617, \end{aligned} \quad (5.2)$$

for which the minimum in $\epsilon(k)$ is $\epsilon(0.78) = 17.2$ and the maximum in $f(k)$ is $f(1.52) = 26.0$. Calculations were made with ion charge $Q = -1$ a.u.

As discussed in the previous section, we applied Bakushinsky regularization in order to overcome instability in the solution of Eqs. (2.4). In order to minimize as much as possible the regions where the solution diverges, while trying to observe the condition $\alpha \rightarrow 0$, a value of $\alpha = 5$ was taken, although even with this value a degree of instability remains. For the purposes of assessing the condition $\alpha \rightarrow 0$, we compare this quantity to $\epsilon_0 = 78.39$ (see Sec. IV). A sample medium charge density $g(R)$ for $a = 1.9 \text{ \AA}$ is shown in Fig. 1, the solvation energy is shown in Fig. 2. We find that even after regularization, $U_s(a)$ oscillates significantly for $a < 2 \text{ \AA}$, with maximal points corresponding to those points where the solution to Eq. (2.4) becomes unstable. The minima however roughly follow the exponential solvation energy of Ref. 1, in which a monotonic susceptibility kernel was applied retaining only the Lorentzian component of Eq. (3.3). Above $a = 2 \text{ \AA}$ the solution appears to be stable.

It would appear that parametrization (5.2) overestimates the strength of the poles. We therefore also considered an-

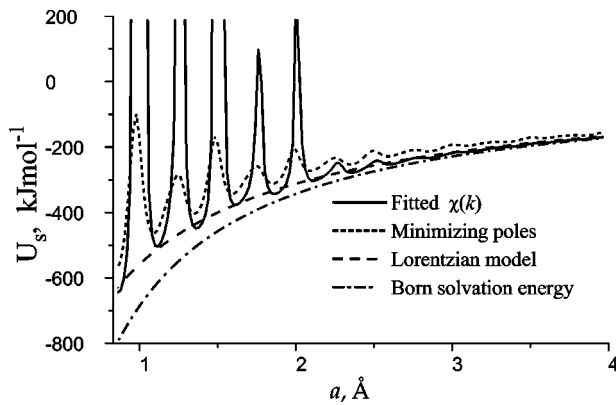


FIG. 2. Electrostatic solvation energy U_s as a function of cavity radius a for a nonlocal electrostatic model with a fixed cavity, using Bakushinsky regularization. Curves shown for parameters fitted to published dielectric function (Ref. 9) (see Eq. (5.2), $\alpha=5$), and minimizing poles [see Eq. (5.3), $\alpha=1$]. Also shown for comparison is the Born solvation energy. Ion charge $=-1$ a.u.

other parametrization of $\chi(k)$ in which the strength of the poles was reduced. The corresponding set of parameters satisfying inequalities (3.5) is

$$\lambda = 10 \text{ \AA}, \quad (5.3)$$

$$\chi_1 = \chi_2 = 1.2 \quad \chi_\infty = 0.0741.$$

Other parameters are as given in Eqs. (5.2). What is lost here compared to Eqs. (5.2) is the magnitude of the minimum in $\chi(k)$ for low k : here $\chi(k=0.686) = 0.19 \ll 1.3$. As to the relevance of this parametrization from the point of view of the MD simulations, we comment only that the minimum for low k found in Ref. 9 had a high degree of uncertainty, and it is not entirely clear what the true behavior of $\chi(k)$ is in this region. We find that with this parametrization, instability in the solution to Eq. (2.4) is much milder, in the sense that calculations may be successfully made with a significantly smaller Bakushinsky parameter (we took here $\alpha=1.0$). The medium charge density retains its oscillatory character (Fig. 1). Similarly the solvation energy contains slightly milder oscillations, as shown in Fig. 2. These oscillations could be made milder still, by reducing the weights of the poles χ_1 and χ_2 further, but this would violate the stability criteria.

VI. NONRIGID CAVITY MODEL

Oscillations in the solvation energy $U_s(a)$ as a function of cavity radius a still exist even in the best calculations of Sec. V. Although no direct evidence can be presented that such oscillations are an artifact of the cavity model, it seems desirable to be able to obtain a smoother function and also to provide a physical basis for applying the regularization procedure. To this end we extend further the cavity model by making an allowance for changes in the radius a . A discussion of this assumption and its consequences can be found in the recent literature.^{20–23}

The main idea is introduced in terms of the variational principle. In Ref. 1 we considered the free energy functional (FEF) $U[M]$, where the total medium field

$$M(\mathbf{r}) = \xi(\mathbf{r}) + \Phi(\mathbf{r}) \quad (6.1)$$

was assumed to be an independent variable. In the purely electrostatic FEF,

$$U[M] = \Sigma[M] + W[M], \quad (6.2)$$

the first (the self-energy) and the second (the interaction energy) contributions are defined as

$$\Sigma[M] = \frac{1}{8\pi} \int d^3\mathbf{r} (\nabla\varphi)^2 - \frac{1}{8\pi} \int d^3\mathbf{r} \nabla\Psi(\hat{\epsilon}\nabla\Psi), \quad (6.3)$$

$$W[M] = \int d^3\mathbf{r} \rho M,$$

where $\rho(\mathbf{r})$ is the solute charge density, vanishing outside the cavity. Equations (2.4) were obtained from the variational condition

$$\frac{\delta U}{\delta M} = 0. \quad (6.4)$$

The energy expression (2.7) is obtained as a minimum in the FEF (6.2) when equilibrium solutions to Eqs. (2.4), $g(R) = g_{\text{eq}}(R)$ and $\sigma = \sigma_{\text{eq}}$ are inserted to obtain $M(\mathbf{r})$.

Let us now consider the cavity radius a as a new variable complementary to the continuum field variable $M(\mathbf{r})$. The corresponding extended FEF has the general form

$$\mathcal{L}[M(\mathbf{r}), a] = U[M(\mathbf{r})] + \Delta(a) + \mathcal{A}[M(\mathbf{r}), a]. \quad (6.5)$$

Here $\Delta(a)$ is a portion of the free energy associated with the cavity variable a and is therefore independent of M . \mathcal{A} is the interaction term, considered to be linear in M :

$$\mathcal{A}[M, a] = \int_{V_e} d^3\mathbf{r} \rho_e M. \quad (6.6)$$

The quantity $\rho_e(\mathbf{r})$ has the dimensions of charge density ($\rho_e = 0$ for $\mathbf{r} \in V_i$). It depends on a but not on M . Its interaction with the external charge ρ ($\rho = 0$ for $\mathbf{r} \in V_e$) generates the energy term

$$\delta = \frac{1}{2} \int d^3\mathbf{r} \rho_e \varphi, \quad (6.7)$$

where φ is the vacuum potential of ρ :

$$\nabla^2 \varphi = \begin{cases} -4\pi\rho & (\mathbf{r} \in V_i) \\ 0 & (\mathbf{r} \in V_e) \end{cases}. \quad (6.8)$$

The variational condition for the FEF (6.5) reads

$$\frac{\delta \mathcal{L}}{\delta M} = 0, \quad \frac{\partial \mathcal{L}}{\partial a} = 0. \quad (6.9)$$

The corresponding equilibrium equations are obtained as shown previously in Sec. III of Ref. 1. For the electric fields, the explicit result is:

$$\nabla(\hat{\epsilon}\nabla\Psi) = -4\pi\rho_e \quad (\mathbf{r} \in V_e), \quad (6.10)$$

$$\nabla^2\Psi = -4\pi\rho \quad (\mathbf{r} \in V_i)$$

with the same nonlocal boundary conditions as in the purely electrostatic case. By inserting the corresponding equilibrium solution for given a , $M_{\text{eq}}(\mathbf{r}|a) \equiv M_{\text{eq}}$, the following expression for the self-energy Σ may be found:

$$\Sigma[M_{\text{eq}}] = -\frac{1}{2} \int_{V_i} d^3\mathbf{r} \rho M_{\text{eq}} - \frac{1}{2} \int_{V_e} d^3\mathbf{r} \rho_e M_{\text{eq}} - \delta. \quad (6.11)$$

The method for obtaining Eq. (6.11) is traced in Ref. 1. The corresponding electrostatic component of the (equilibrium) solvation energy is

$$\begin{aligned} U_s(a) &= U[M_{\text{eq}}] + \mathcal{J}[M_{\text{eq}}, a] \\ &= \frac{1}{2} \int_{V_i} d^3\mathbf{r} \rho M_{\text{eq}} + \frac{1}{2} \int_{V_e} d^3\mathbf{r} \rho_e M_{\text{eq}} - \delta. \end{aligned} \quad (6.12)$$

Here δ is given by Eqs. (6.7) and (6.8).

The equilibrium condition for a (the second condition in (6.9)) gives

$$\frac{\partial U_s(a)}{\partial a} + \frac{\partial \Delta(a)}{\partial a} = 0. \quad (6.13)$$

The root of this equation is denoted as $a = a_{\text{eq}}$. Finally, we find the total solvation energy by inserting M_{eq} and a_{eq} in Eq. (6.5):

$$\begin{aligned} \mathcal{L}_s &= \mathcal{L}[M_{\text{eq}}, a_{\text{eq}}] \\ &= U_s(a_{\text{eq}}) + \Delta(a_{\text{eq}}). \end{aligned} \quad (6.14)$$

This concludes the computational scheme suggested by the nonrigid model.

VII. SPECIFICATION OF THE INTERACTION TERM

We now need to determine the equations defining the charge densities $g(R)$ and σ . They are derived from the basic equations (6.10) and the boundary conditions. The derivation here follows our earlier reasoning,^{1,6} and, for the present spherical model, gives the result:

$$\begin{aligned} g(R) + \frac{4\pi}{\epsilon_\infty} \int_a^\infty dR' \gamma(R, R') g(R') \\ = -\frac{1}{\epsilon_\infty} \left(\frac{Q}{a^2} + 4\pi\sigma \right) \gamma(R, a) + \frac{\rho_e(R)}{\epsilon_\infty}. \end{aligned} \quad (7.1)$$

This equation differs from the equation defining $g(R)$ in the purely electrostatic theory, Eq. (2.4), only by the last term $\rho_e(R)/\epsilon_\infty$. The equation for σ remains unchanged, given by the second equation in (2.4).

It is now in order to make a choice for the charge $\rho_e(R)$. This is the central point of our treatment. The suggested expression is

$$\rho_e(R) = \frac{\alpha^2}{(I + 4\pi/\epsilon_\infty \hat{\Gamma})^2 + \alpha^2} \left[\left(\frac{Q}{a^2} + 4\pi\sigma \right) \gamma(R, a) \right]. \quad (7.2)$$

Here operator $\hat{\Gamma}$ and constant α have been borrowed from the regularization procedure of Sec. IV (Eqs. (4.2) and (4.6)), with the important difference that α is now an explicit parameter of the theory and is no longer required to go strictly to zero. The idea of the present ansatz is that by inserting Eq. (7.2) into Eq. (7.1) for $g(R)$, we reduce the latter to the regularized form of Eq. (4.7):

$$g(R) = \frac{\hat{A}}{\hat{A}^2 + \alpha^2 I} f(R), \quad (7.3)$$

$$f(R) = -\frac{1}{\epsilon_\infty} \left(\frac{Q}{a^2} + 4\pi\sigma \right) \gamma(R, a),$$

where $\hat{A} = I + 4\pi\hat{\Gamma}$. For by multiplying Eqs. (7.3) by \hat{A} we obtain

$$\hat{A}g(R) = f(R) - \frac{\alpha^2}{\hat{A}^2 + \alpha^2 I} f(R) \quad (7.4)$$

which is identical with Eq. (7.1) provided ρ_e is given by Eq. (7.2). Thereby the regularization procedure is explicitly incorporated into the theory.

It is appropriate here to take a step back in order to explain the present phenomenological approach. Its basic idea is that the interaction term $\mathcal{J}[M(\mathbf{r}), a]$ in Eq. (6.5) removes singularities inherent to the purely electrostatic FEF component $U[M(\mathbf{r})]$ by coupling the polarization field $M(\mathbf{r})$ with the cavity variable a . The strength of this coupling, given by the pseudo-charge $\rho_e(\mathbf{r})$, is an empirical quantity which must be specially fitted to the oscillating purely-electrostatic medium response $g(R)$ so as to cancel the singularities generated by the latter. The mechanism which creates a relationship between the two charge functions $g(R)$ and $\rho_e(R)$ is established by the combination of Eqs. (7.1) and (7.2), which results in the appearance of Eq. (7.4) without singularities. In all, the procedure involves a single empirical parameter α , a measure of the coupling strength, whose choice of value is expected to result in a smooth equilibrium free energy \mathcal{L} , as a function of solute ionic radius.

The actual computation proceeds as follows. In solving Eq. (7.1) we are effectively solving the equation in $g(R)$ given in Eq. (7.3) where α is a parameter. The expression for ρ_e is not strictly necessary at this stage. It is only required when the corresponding energy contribution in Eq. (6.12) is evaluated. Then calculation of ρ_e by Eq. (7.2) becomes in fact essential, which is actually the solution of another integral equation similar to Eq. (7.3). Note that in both Eqs. (7.2) and (7.3) only the inversion of positive-definite operators is required. This eliminates the problem of divergency.

VIII. REARRANGEMENT OF ENERGY CONTRIBUTIONS

It is now expedient to rearrange the energy contributions to the FEF (6.5):

$$\begin{aligned} \Sigma'(a) &= \Sigma(a) + \delta(a), \\ U'(a) &= U(a) + \delta(a), \\ \Delta'(a) &= \Delta(a) - \delta(a). \end{aligned} \quad (8.1)$$

Here δ is formally interpreted, according to Eq. (6.7), as an interaction between charges ρ and ρ_e . It is important to comment that ρ_e is not a true charge because, according to Eq. (6.8), it makes no contribution to the vacuum field $\varphi(\mathbf{r})$. One can make the comment that ρ_e interacts with the polarization field (Eq. (6.6)) but not with the external solute

charge ρ . We see in Eqs. (6.11) and (6.12) that the corresponding interaction energy δ has been subtracted from the equilibrium electrostatic energy terms. According to Eqs. (8.1), we transfer this contribution back to the electrostatic energy $U(a)$, taking it from the cavity energy $\Delta(a)$. This is formally legitimate since $\delta(a)$ does not depend on M and so may be ascribed to $\Delta(a)$.

We thereby define the new equilibrium electrostatic energies:

$$\Sigma'[M_{\text{eq}}] = -\frac{1}{2} \int d^3r M_{\text{eq}}(\rho + \rho_e), \quad (8.2)$$

$$U'_s(a) = \frac{1}{2} \int d^3r M_{\text{eq}}(\rho + \rho_e),$$

so that instead of Eq. (6.14), we have

$$\mathcal{L}[M_{\text{eq}}, a] = U'_s(a) + \Delta'(a). \quad (8.3)$$

We shall refer to the two contributions entering Eq. (8.3) as the electrostatic solvation energy and the cavitation energy, respectively.

It should be stressed that, because δ is M -independent,

$$\frac{\delta \Sigma}{\delta M} = \frac{\delta \Sigma'}{\delta M}, \quad \frac{\delta U}{\delta M} = \frac{\delta U'}{\delta M}, \quad (8.4)$$

and the variational equations of Secs. VI and VII remain unchanged. Only the new definition of the cavitation term is truly important. This term will now be treated on purely empirical grounds. We expect that the cavitation energy has a minimum at some point $a = a_0$ where $\partial \Delta' / \partial a = 0$. Therefore we assume

$$\Delta'(a) = \frac{b}{2}(a - a_0)^2 + \Delta'(a_0). \quad (8.5)$$

The constant last term is neglected in purely electrostatic solvation models and we also make this assumption. The quantities b and a_0 are treated as empirical parameters. A natural interpretation for a_0 is as an intrinsic radius of a given spherical ion, a standard parameter met in the majority of solvation theories. In the nonrigid cavity model it should be distinguished from the equilibrium radius, obtained as the root of the equation that follows from Eqs. (6.13), (8.3) and (8.5):

$$\frac{\partial U'_s}{\partial a} + b(a - a_0) = 0. \quad (8.6)$$

This value $a = a_{\text{eq}}$ is inserted into Eq. (8.3), ultimately giving the total solvation energy

$$\mathcal{L}_s = \mathcal{L}[M_{\text{eq}}, a_{\text{eq}}] = U'_s(a_{\text{eq}}) + \Delta'(a_{\text{eq}}). \quad (8.7)$$

The assignment of energy terms according to Eq. (8.1) is made on purely empirical grounds. In this way the fictitious interaction term δ (Eq. (6.7)) disappears from calculations. With other definitions it would contribute to the calculated solvation energy, but this is undesirable because, as shown by numerical tests for the parametrization in Eq. (5.2), it is capable of being much larger than other terms and the respective results become unsatisfactory.

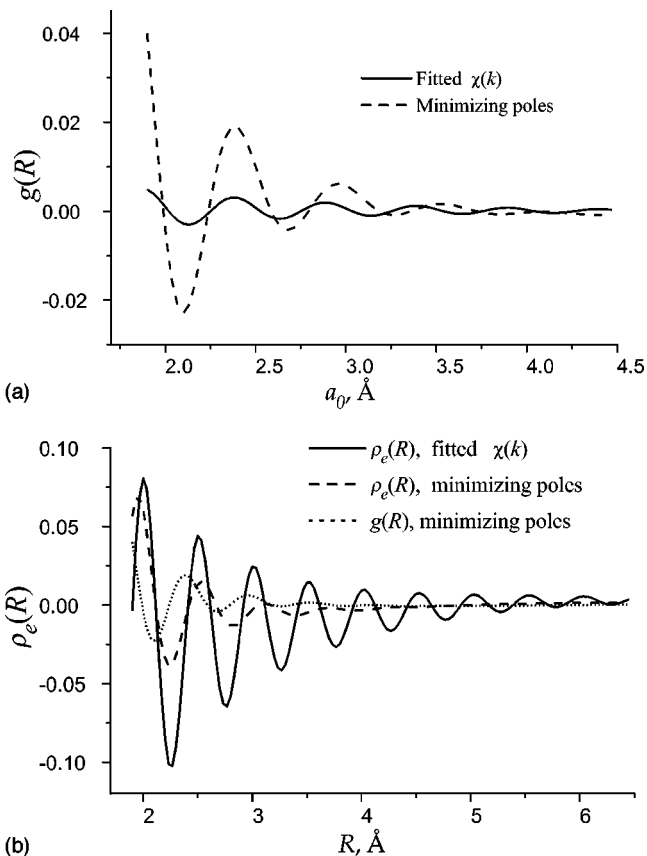


FIG. 3. Sample charge distributions (10^9 V m^{-1}) for a nonlocal electrostatic model of water with a nonrigid cavity, using parameters (i) fitted to published dielectric function (Ref. 9), see Eq. (5.2), $\alpha = 15$, and (ii) minimizing poles, see Eq. (5.3), $\alpha = 1$. Shown are (a) induced medium charge distribution $g(R)$ and (b) supplementary charge distribution $\rho_e(R)$ (together with $g(R)$ for case (ii) for comparison of scale). Cavity radius $a = 1.9 \text{ \AA}$. Ion charge = -1 a.u.

The crucial point of this empirical prescription is our assumption that function $\Delta'(a)$, defined according to Eq. (8.1), has a minimum $a = a_0$ which is identified with the experimental ion radius. This can be tested only within a microscopic cavitation model. Possible inconsistencies are hidden in this assumption, but after it is accepted the formal treatment becomes internally consistent.

IX. TEST CALCULATIONS FOR THE NONRIGID CAVITY MODEL

Calculations were made using the same two parametrization sets used in Sec. V, Eqs. (5.2) and (5.3). There is here no strict requirement to set $\alpha \rightarrow 0$, and α was chosen to be as small as possible such that no irregular behavior appeared in the electrostatic solvation energy U'_s . This led to a value of $\alpha = 15$ for the optimized parametrization of Eq. (5.2) (larger than the value $\alpha = 5$ applied in Sec. V), and the same value $\alpha = 1.0$ for parametrization (5.3) with minimized poles.

Qualitatively, results for $g(R)$, shown in Fig. 3(a), are similar to those found in Sec. V (see Fig. 1). Sample results for $\rho_e(R)$ are given in Fig. 3(b), with $g(R)$ from parametrization (5.3) given for comparison of scale. We notice that $\rho_e(R)$ has a similar appearance to $g(R)$, the relative magnitude of these two functions for a given calculation depends

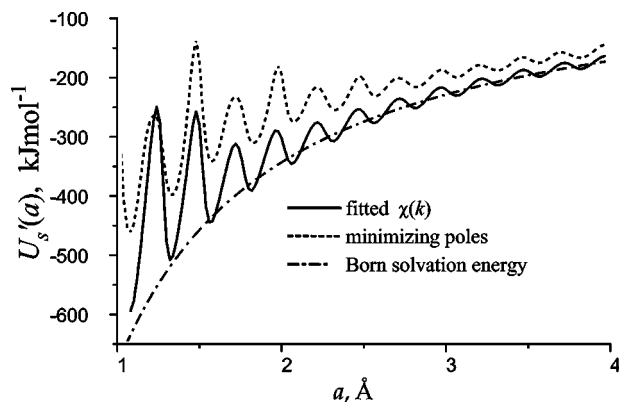


FIG. 4. Electrostatic solvation energy U'_s as a function of cavity radius a for a nonlocal electrostatic model with a nonrigid cavity. Curves shown for parameters fitted to published dielectric function (Ref. 9) [see Eq. (5.2), $\alpha = 15$], and minimizing poles [see Eq. (5.3), $\alpha = 1$]. Also shown for comparison is the Born solvation energy. Ion charge = -1 a.u.

on the size of the interaction parameter α . That is, for parametrization (5.2) with $\alpha = 15$, $\rho_e(R)$ is much larger than $g(R)$, while for parametrization (5.3) with $\alpha = 1$, $\rho_e(R)$ was of a comparable size to $g(R)$.

The electrostatic solvation energy $U'_s(a)$, shown in Fig. 4, was also similar to $U_s(a)$ in Sec. V. The main difference was found in having the freedom to give the interaction parameter α a value far from zero ($\alpha = 15$ for parametrization (5.2)), which enabled us to remove the strong oscillations that appeared in Fig. 2. Note that the fact that the oscillations increase in strength with decreasing cavity radius, observed also in Sec. V for calculations with a fixed cavity, shows that the interaction between the electrostatic field and cavity variables becomes stronger the smaller the cavity size. We report this here as an empirical observation. Although it seems obvious that small solutes are particularly difficult objects for a continuum theory, further study of this effect in terms of combined molecular and continuum treatments is desirable.

In the final stage, applying the cavitation energy $\Delta'(a)$, Eq. (8.5), in order to remove the oscillations altogether, experience showed that best smoothing was obtained if the cavitation parameter b was inversely dependent on the intrinsic ion radius a_0 . We took

$$b = \frac{4000}{a_0^2}. \quad (9.1)$$

The units of the empirical constant 4000 are $\text{kJ mol}^{-1} \text{\AA}^{-2}$. This value was chosen so as to ensure that the free energy \mathcal{Z} is a smooth function following the minima of U'_s . For larger values, the free energy \mathcal{Z} would start following the oscillations of U'_s , for smaller values it would be monotonic but with a large shift away from the minima of U'_s . Note that we neglect here the constant $\Delta'(a_0)$ in Eq. (8.5), as mentioned above. Final results for the solvation free energy $\mathcal{Z}(a_0)$ are shown in Fig. 5, with the electrostatic solvation energy $U'_s(a_0)$ for the second parametrization (5.3) shown for comparison together with the solvation energy determined by a purely Lorentzian model of $\chi(k)$ ($\lambda = 4.83 \text{\AA}$, fitted to experimental values¹). Also given are molecular dynamics and

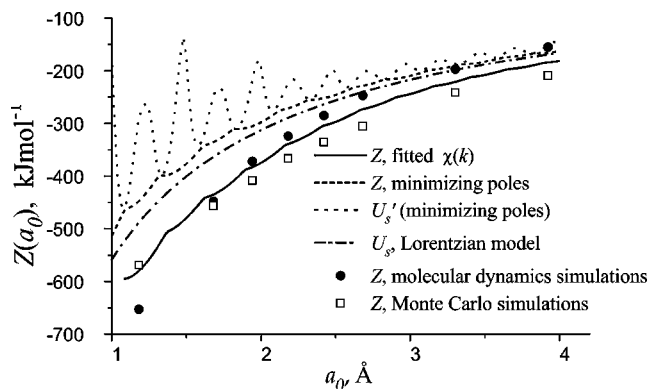


FIG. 5. Free energy function $\mathcal{Z}(a_0)$, with cavitation parameter b depending on ion radius a_0 (see the text). Units of b are $\text{kJ mol}^{-1} \text{\AA}^{-2}$. Curves shown for parameters fitted to the published dielectric function (Ref. 9) ($\lambda = 2.95 \text{\AA}$, $\chi_1 = \chi_2 = 0.209$, $\alpha = 15$), and minimizing poles ($\lambda = 10.0 \text{\AA}$, $\chi_1 = \chi_2 = 0.074$, $\alpha = 1$). Electrostatic solvation energy $U'_s(a_0)$ for the latter is also shown for comparison, along with the solvation energy produced by a purely Lorentzian model of $\chi(k)$, fitted to experimental values ($\lambda = 4.83 \text{\AA}$). Circular dots correspond to molecular dynamics simulation data for anions in water, and square boxes to Monte Carlo simulations, taken from Ref. 26. Solvation free energy is half the "average solvation energy" in Fig. 1 of the latter.

Monte Carlo simulation data for anions in water.²⁶ We notice that there is fair agreement between these data and our solvation free energy curve as produced by our first parametrization (5.2), in which the dielectric function $\chi(k)$ was fitted to that given by other molecular dynamics simulations. Our curve is situated between the two simulation curves, slightly closer to the Monte Carlo data. This would seem to demonstrate the consistency of the present continuum solvation theory with molecular dynamics calculations. A more accurate fitting of parameters α and b may enable a better agreement to be obtained.

One comment worth making here concerns the relative magnitude of the continuum theory free energy curves. The curve due to Eq. (5.2), with smaller λ (2.95\AA) is of a larger magnitude than the curve with minimized poles ($\lambda = 10.0 \text{\AA}$). Furthermore the experimentally fitted curve calculated from a Lorentzian model, with intermediate $\lambda = 4.83 \text{\AA}$, lies between these two equilibrium free energy curves. This suggests that experimentally relevant results may be procured (assuming cavity radii are reasonable; Rashin-Honig values²⁷ were used in Ref. 1) by fitting only the length parameter λ in the model (3.3), and choosing pole parameters in the manner prescribed in Sec. V, namely, matching the maximum in the function $1 - 1/\epsilon(k)$ and observing stability criteria (3.5), without paying close attention to the minimum in $\chi(k)$ for low k (which is in any case an uncertain quantity). For instance, choosing $\lambda = 4.83 \text{\AA}$ would suggest $\chi_1 = \chi_2 = 0.111$. This differs from Eq. (5.2) in that the low- k minimum for $\chi(k)$ has a much smaller value than 1.3, and could be expected to yield a final solvation free energy curve, $\mathcal{Z}(a_0)$, closer to experimental values (represented in Fig. 5 by the Lorentzian model) than the curves produced by the two parametrizations considered in this paper.

The equilibrium radii a_{eq} obtained using this procedure are found to be smaller than the initial radii a_0 , as observed previously in the literature.²³ In Table I the equilibrium radii

TABLE I. Equilibrium cavity radii a_{eq} for halogen anions as determined by the nonrigid cavity procedure, compared with intrinsic radii a_0 [Pauling radii (Ref. 28)]. Equilibrium radii are presented as calculated from both parametrization schemes: (i) Fitted to $\chi(k)$, Eq. (5.2). (ii) Minimizing poles, Eq. (5.3).

Ion	F ⁻	Cl ⁻	Br ⁻	I ⁻
a_0 (Å)	1.35	1.81	1.96	2.15
a_{eq} (Å), i) fitted $\chi(k)$	1.08	1.58	1.82	2.05
a_{eq} (Å), ii) min. poles	1.34	1.59	1.84	2.08

for halogen anions found using both parametrizations considered here are compared with initial radii. The latter were assumed to be the Pauling radii, as is commonly accepted in studying solvation effects.²⁸

X. DISCUSSION: CONVERGENCE, STABILITY, AND THE VALIDITY OF LORENTZIAN NONLOCAL MODELS OF SOLVATION

The convergence problem encountered in the present work originated from the oscillating nature of the susceptibility kernel $\chi(|\mathbf{r}-\mathbf{r}'|)$. The solution to the basic integral equation of the nonlocal theory involves inversion of the operator $\hat{A} = I + 4\pi\hat{\Gamma}$ [see Eq. (4.1)], which fails to be positive-definite due to the oscillations. As a result, near-zero eigenvalues of \hat{A} cannot be avoided, which leads to the appearance of singularities. Our efforts in Secs. IV–VIII were aimed at restoring the basic property of positive definiteness of this operator using regularization procedures.

The problems of convergence and instability are interrelated. The solvation energy can be expressed in a general way as a quadratic functional of $\rho(\mathbf{r})$:

$$U_s = -\frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \rho(\mathbf{r}) \mathcal{B}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}'), \quad (10.1)$$

which follows from Eq. (2.7) since both $\xi(\mathbf{r})$ and $\Phi(\mathbf{r})$ are linear functionals of $\rho(\mathbf{r})$. The kernel $\mathcal{B}(\mathbf{r}, \mathbf{r}')$ is symmetric and the condition for stability means that it must be positive definite, i.e. has only a positive spectrum of eigenvalues. This property replaces the stability conditions of (3.5), which are meaningful only for a uniform medium. For a system with an excluded cavity it is not easy to formulate simple stability criteria in terms of function $\chi(k)$. It can be shown, however, that the positive-definiteness of kernel $\mathcal{B}(\mathbf{r}, \mathbf{r}')$ is closely connected to the same property of operator \hat{A} and consequently to oscillations in $\chi(|\mathbf{r}-\mathbf{r}'|)$.

As shown recently,⁸ the poles of function $\chi(k)$, which give rise to the oscillations in real space, appear due to a coupling between polarization and density fluctuations in a solvent. This introduces a physical argument into our discussion. The role of density fluctuations has been discussed in recent literature.^{8,29–32} We have considered a mechanism for quenching instabilities by introducing the cavity size as a new dynamical variable. Its fluctuations are strongly correlated to density fluctuations in the solute environment, acting so as to counterbalance the influence of the latter on polarization fluctuations. The corresponding equations defining equilibrium electric fields in systems with an excluded vol-

ume only involve the inversion of renormalized positive-definite integral operators and so have regular solutions.

Therefore the advanced model described in Secs. VI–VIII provides a fine mechanism for suppressing the effect of density fluctuations. The same result is obtained by simply assuming the susceptibility kernel to follow a purely Lorentzian form, which results in the total elimination of density fluctuations. The most significant loss made here is a loss of the oscillatory behavior of function $g(R)$.

Such an approximation, with the cavity radius kept constant, is known to be efficient for the limited purpose of describing the solvation energy. The quantity U_s is insensitive to the fine details of function $g(R)$, whose oscillations seem to bring little contribution to the values of medium potentials $\xi(\mathbf{r})$ and $\Phi(\mathbf{r})$ inside the cavity. For instance, for the spherically symmetric case these potentials are constant irrespective of the shape of $g(R)$.⁶ By accepting this simplified approach one should bear in mind that the Lorentzian kernels $\chi(k)$ thus represent not only a property of a pure solvent but also incorporate a mechanism of solute-solvent interaction via cavity changes. It follows, therefore, that determining the parametrization of these Lorentzian models from the properties of a pure solvent, as is usually the case, is not in fact a consistent procedure. With this reservation, the present discussion may serve as a reasonable justification for utilizing the simple exponential nonlocal solvation theories.

ACKNOWLEDGMENTS

The research was made possible in part by Award No. RC1-202 of the U.S. Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF) and by the International Association for the Promotion of Cooperation with Scientists from the New Independent States of the Former Soviet Union (project INTAS-RFBR 95-0182). M.V.B. also acknowledges financial support from the Russian Foundation for Basic Research (Grant Nos. 96-03-32544 and 96-15-97465).

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