

# Molecular Basis for the Born Model of Ion Solvation

Benoit Roux, Hsiang-Ai Yu, and Martin Karplus\*

Department of Chemistry, Harvard University, 12 Oxford St., Cambridge, Massachusetts 02138

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Statistical mechanical theory of aqueous solutions is used to provide an interpretation for the Born model of ion hydration at the molecular level. The analysis is based on an asymptotic solution to the extended RISM integral equation in the limit of a large spherical solute. It is shown that a construction of the appropriate direct correlation function yields the Born model for the electrostatic free energy of solvation. In this approximation the free energy of solvation equals half the average solute-solvent interaction energy. Results of the RISM-HNC calculations for microscopic ions as a function of charge are presented, and the Born radius of hydration is interpreted in terms of the first peak in the solute-solvent radial distribution function: in water this leads to different radii for positive and negative ions. Analysis indicates that the Born model gives the dominant contribution to the free energy of charging a microscopic ion in water but that it is not appropriate for the calculation of solvation enthalpies because of their sensitivity to the temperature dependence of the Born radius.

## 1. Introduction

The properties of polar solvents, particularly water, play an essential role in chemistry and biology.<sup>1</sup> Although detailed atomic models are needed for a full understanding of solvation, simpler phenomenological models are useful to interpret the results for complex systems. One such model, originally proposed by Born to calculate the excess free energy of solvation of spherical ions,<sup>2</sup> is based on classical electrostatics and represents the solvent as a structureless dielectric continuum. Extensions of Born-type models to more complex geometries have been used in recent applications of classical continuum electrostatics to macromolecular systems.<sup>3-6</sup>

For a spherical ion, the Born excess free energy of solvation,  $\Delta\mu$ , has a very simple dependence on the ionic charge  $Q$ , the radius  $\sigma$ , and the solvent dielectric constant  $\epsilon$ :

$$\Delta\mu = \frac{Q^2}{2\sigma} \left( \frac{1}{\epsilon} - 1 \right) \quad (1.1)$$

While there is no doubt that the Born model retains some of the fundamental features of polar solvents, the microscopic interpretation of the parameters in (1.1), particularly the radius  $\sigma$ , remains uncertain.

Chan et al.<sup>7</sup> used the mean spherical approximation model (MSA) to show that the excess chemical potential of a charged hard sphere immersed in a hard-sphere solvent with an embedded point dipole can be expressed as a modified form of the Born equation; i.e., they obtained (1.1) with  $\sigma$  replaced by  $\sigma = R_{\text{ion}} + R'_{\text{solvent}}$ , where  $R_{\text{ion}}$  is the hard-sphere radius of the ion and  $R'_{\text{solvent}}$  is a length that depends on the solvent hard-sphere radius, density, temperature, and dipole moment. This expression is reminiscent of a formula that had been used empirically to fit solubility data<sup>8</sup> and suggests that the concept of continuum electrostatics is valid even on a microscopic-length scale.

Models that represent atoms and molecules as pair decomposable soft-core interaction sites, such as those used in modern computer simulations,<sup>9</sup> are thought to provide a more realistic description of the microscopic chemistry than does the hard-sphere point dipole model. Extended reference interaction site method (RISM) calculations<sup>10,11</sup> using such realistic model ions in aqueous

solution have shown that the excess chemical potential of ions is approximately equal to half of the average ion-solvent interaction energy and that it increases quadratically with the ionic charges. These observations are consistent with the linear dielectric response used in the Born model. Similar agreement with the Born model of solvation has been observed and reported in recent Monte Carlo<sup>9</sup> and molecular dynamics simulations.<sup>12,13</sup>

This communication clarifies the reasons for the agreement between realistic microscopic models and the Born equation. Our analysis is based on an asymptotic solution to the extended RISM integral equation (i.e., with the site-site hypernetted chain (HNC) closure)<sup>14-16</sup> in the limit of large solute size compared to solvent size. It is shown that a form of the direct correlation function can be found that leads to the Born equation. Further, a simple relation between the free energy of solvation and the average electrostatic solute-solvent interaction energy is demonstrated. To complete the analysis, results of RISM-HNC calculations for ions as a function of charge are presented and the Born radius of hydration is interpreted in terms of the solute-solvent radial distribution function.

## 2. Direct Correlation Function

The RISM equation for a single monatomic solute of charge  $Q$  is<sup>15-17</sup>

$$h_\gamma(r)\rho = \sum_\alpha c_\alpha \chi_{\alpha\gamma}(r) \quad (2.1)$$

For polar ions, (2.1) is supplemented by the HNC closure

$$h_\gamma(r) = e^{-\beta u_\gamma(r) + h_\gamma(r) - c_\gamma(r)} - 1 \quad (2.2)$$

to obtain a pair of equations for the site-site pair correlation function  $h_\gamma(r)$  and the direct correlation function  $c_\gamma(r)$ . The quantity  $\rho$  is the bulk density of the solvent,  $\chi_{\alpha\gamma}$  represents the pure solvent density pair correlation,  $\beta u_\gamma(r)$  is the site-site potential in units of  $k_B T$ , and  $\alpha$  and  $\gamma$  are sites on the solvent molecule (O, H1, and H2 in water). Two subscripts refer to solvent-solvent functions, and those with one subscript refer to the solute-solvent functions.

The purpose of the present analysis is to extract the dominant aspects of the solvation of a charged solute. For a charged solute, the direct correlation function in (2.2) behaves asymptotically like<sup>16</sup>

$$c_\alpha(r) \rightarrow -\frac{\beta Q q_\alpha}{r} \quad (2.3)$$

for large  $r$ . Furthermore, the presence of core repulsion guarantees that

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$$h_\gamma(r) = -1, \quad r < \sigma \quad (2.4)$$

where the core size  $\sigma$  depends, in general, on short- and long-ranged portions of the solute-solvent interaction potential and thermodynamic variables, such as temperature and density. The two conditions (2.3) and (2.4) are sufficient to incorporate the most important aspects of the solute-solvent radial distribution functions. The asymptotic behavior of the direct correlation function (2.3) and the existence of a core condition (2.4) are reproduced by the HNC closure, the Percus-Yevick closure, and by a more complex closure proposed recently.<sup>18</sup> Together, they are reminiscent of the MSA,<sup>14</sup> for which exact analytical solutions have been obtained recently for a polar solvent of fused hard spheres and hard-sphere ions.<sup>19,20</sup> However, the present model is more realistic in that a molecular solvent and soft-sphere radii are used. Further, it is possible to determine  $\sigma$  by detailed calculations.

In the limit of large solute size, an approximate construction of the direct correlation function can be attempted. We assume that the asymptotic form (2.3) is valid for all  $r > \sigma$

$$c_\alpha(r) \simeq -\frac{\beta Q q_\alpha}{r}, \quad r > \sigma \quad (2.5)$$

The assumption of a site-label independent  $\sigma$  is based on the expected irrelevance of solvent molecular structure in the limit of a large solute. The direct correlation function inside the core is assumed, like  $h_\gamma(r)$ , to be a constant; that is

$$c_\alpha(r) \simeq \text{constant}, \quad \text{for } r < \sigma \quad (2.6)$$

For convenience, we write it as a sum of two terms: one is simply the value of the long-range term at  $r = \sigma$  and the other is a constant, independent of the site labels, that is required to satisfy (2.4), as shown below. Thus, we have

$$c_\alpha(r) \simeq A - \frac{\beta Q q_\alpha}{\sigma}, \quad r < \sigma \quad (2.7)$$

The discontinuity at  $\sigma$  introduced by  $A$  is small and would be removed with a site-site closure such as HNC that has a soft-core repulsion.

Given (2.5) and (2.7), the direct correlation function in  $k$  space is

$$\hat{c}_\alpha(k) = \hat{f}(k)A - \frac{\sin(k\sigma)}{k\sigma} \frac{4\pi\beta Q q_\alpha}{k^2} \quad (2.8)$$

where  $\hat{f}(k)$  is the structure factor of a spherical step function ( $f(r) = -1$  for  $r < \sigma$  and  $\hat{f}(k) = 4\pi(\sigma \cos(k\sigma)/k^2 - \sin(k\sigma)/k^3)$ ). In the limit of a large solute, the oscillating terms in (2.8) will vary much more rapidly than any oscillations of the solvent response function  $\hat{\chi}_{\alpha\gamma}(k)$ , which can be approximated by its long-wavelength (small  $k$ ) behavior. For small  $k$ , an expansion of the solvent response function to second order in  $k$  has been shown to be valid under general conditions (away from critical points);<sup>21</sup> the result is

$$\hat{\chi}_{\alpha\gamma}(k) \simeq \hat{\chi}^{(0)} + \hat{\chi}_{\alpha\gamma}^{(2)} k^2 \quad (2.9)$$

where according to the compressibility theorem, the  $k \rightarrow 0$  limit of  $\hat{\chi}_{\alpha\gamma}(k)$  is independent of the site labels  $\alpha$  and  $\gamma$ .<sup>21</sup> Substituting into the  $k$ -space form of (2.1) and keeping only the dominant terms (lowest order in  $k$ ), we find

$$\begin{aligned} \hat{h}_\gamma(k)\rho &= \hat{f}(k) \sum_\alpha A \hat{\chi}^{(0)} - 4\pi\beta Q \frac{\sin(k\sigma)}{k\sigma} \sum_\alpha q_\alpha \hat{\chi}_{\alpha\gamma}^{(2)} \\ &= \hat{f}(k) n A \hat{\chi}^{(0)} - 4\pi\beta Q \frac{\sin(k\sigma)}{k\sigma} \sum_\alpha q_\alpha \hat{\chi}_{\alpha\gamma}^{(2)} \end{aligned} \quad (2.10)$$

where the electroneutrality of the solvent ( $\sum_\alpha \hat{\chi}^{(0)} q_\alpha = 0$ ) has been used. The constant  $A$  is determined by the core requirement, (2.4); i.e.,  $n A \hat{\chi}^{(0)} / \rho = 1$ , where  $n$  is the total number of sites in a solvent

molecule.  $A$  is about  $-2.8$  for the TIPS3P water model. The presence of  $A$  has a negligible effect and introduces only a relatively small discontinuity in the direct correlation function, since  $c(r)$  as given by (2.7) is of the order 100–300 in the core region for  $\sigma$  in the range 3–2 Å. Considering (2.10) in  $r$  space

$$h_\gamma(r)\rho = f(r) - \beta Q \frac{\delta(r-\sigma)}{r^2} \sum_\alpha q_\alpha \hat{\chi}_{\alpha\gamma}^{(2)} \quad (2.11)$$

we see that the first term, by design, fulfills the core condition (2.4), while the second term produces a sharp peak at  $\sigma$  corresponding to the first peak in the radial distribution function (a  $\delta$  function for this approximate solution).

### 3. Excess Chemical Potential

Having constructed an approximate direct correlation function valid for large  $\sigma$ , we can evaluate the excess chemical potential for a charged spherical solute. The excess chemical potential can be calculated via the "charging" procedure<sup>17</sup>

$$\Delta\mu = \int_0^Q dQ' \int d^3r (\sum_\gamma h_\gamma(r;Q') \rho q_\gamma) \frac{1}{r} \quad (3.1)$$

where  $h_\gamma(r;Q')$  is the equilibrium distribution function around a solute with a charge  $Q'$ . Transforming the integral to  $k$  space, we have

$$\Delta\mu = \int_0^Q dQ' \int \frac{d^3k}{(2\pi)^3} (\sum_\gamma \hat{h}_\gamma(k;Q') \rho q_\gamma) \frac{4\pi}{k^2} \quad (3.2)$$

With (2.10), this expression becomes

$$\Delta\mu = \int_0^Q dQ' Q' \left( \frac{1}{\epsilon} - 1 \right) \frac{(4\pi)^2}{(2\pi)^3} \int_0^\infty \frac{\sin(k\sigma)}{k\sigma} dk \quad (3.3)$$

Evaluation of the integral leads to

$$\Delta\mu = \left( \frac{1}{\epsilon} - 1 \right) \int_0^Q dQ' \frac{Q'}{\sigma(Q';T,\rho)} \quad (3.4)$$

where the pure solvent dielectric constant  $\epsilon$  is related to the  $\hat{\chi}_{\alpha\gamma}^{(2)}$  by<sup>21</sup>

$$\left( \frac{1}{\epsilon} - 1 \right) = -4\pi\beta \sum_{\alpha,\gamma} q_\alpha \hat{\chi}_{\alpha\gamma}^{(2)} q_\gamma \quad (3.5)$$

To obtain a simple expression, it is necessary to assume that the effective Born radius,  $\sigma(Q';T,\rho)$ , in (3.4) is independent of the solute charge. This approximation is appropriate for large solute size, though it appears to be valid for microscopic ions as well (see below). The excess chemical potential is then simply

$$\Delta\mu = \frac{Q^2}{2\sigma} \left( \frac{1}{\epsilon} - 1 \right) \quad (3.6)$$

This expression can be recognized as the Born free energy of transfer for an ion of radius  $\sigma$  from vacuum to a continuum of dielectric constant  $\epsilon$ .<sup>2</sup> The value of the dielectric constant  $\epsilon$  in (3.5) and (3.6) depends on the particular pure solvent density pair correlation used in (2.1). In RISM calculations, the dielectric constant  $\epsilon$  takes the ideal gas value when the solvent structure is obtained from the HNC closure.<sup>21</sup> Alternatively, it is possible to use the experimental dielectric constant of the solvent as an input to a modified HNC closure to construct  $\hat{\chi}_{\alpha\gamma}^{(2)}$  yielding the proper  $\epsilon$ .<sup>22,23</sup>

A corresponding analysis enables us to clarify the origin of an empirical relationship between the total solute-solvent electrostatic interaction energy and the solvation free energy for polar and ionic systems.<sup>10,23</sup> The former is given by

$$\langle U_{\text{elec}}(Q) \rangle = \int d^3r (\sum_\gamma h_\gamma(r;Q) \rho q_\gamma) \frac{Q}{r} \quad (3.7)$$

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Using arguments similar to those leading to (3.6) to evaluate (3.7), we find

$$\Delta\mu(Q) = \frac{1}{2} \langle U_{\text{elec}}(Q) \rangle \quad (3.8)$$

in agreement with the empirical result.<sup>10</sup>

A linear response of the solvent to a charged solute is embodied in the Born equation. That it can be obtained from a full statistical mechanical treatment is a striking result. However, it must be noted that our analysis is based on an effective Born radius  $\sigma$  that is charge independent. This assumption, which is used to go from (3.4) to (3.6), appears not to hold for a small solute with a large charge (e.g.,  $\text{Fe}^{3+}$ ).<sup>11</sup>

To gain further insight into the origin of the Born excess free energy, it is useful to consider the relationship between the solvent structure in the vicinity of the solute and the long-range behavior of the effective electrostatic potential at a large distance from the solute. In the solvent, the potential varies asymptotically as  $\sim Q/\epsilon r$  for large  $r$ ,<sup>21</sup> relative to  $Q/r$  for a charge in vacuo; this is in accord with the form obtained from the HNC closure.<sup>24</sup> Such an asymptotic behavior imposes a constraint on  $\rho_{\text{elec}}(r;Q)$ , the net solvent charge density induced by an ion in its neighborhood, which has the form

$$\rho_{\text{elec}}(r;Q) = \sum_{\gamma} h_{\gamma}(r;Q) \rho q_{\gamma} \quad (3.9)$$

By use of the asymptotic condition and Gauss's theorem,  $\rho_{\text{elec}}(r;Q)$  obeys the sum rule

$$\begin{aligned} \int d^3r \sum_{\gamma} h_{\gamma}(r;Q) \rho q_{\gamma} &= \int d^3r \rho_{\text{elec}}(r;Q) \\ &= Q \left( \frac{1}{\epsilon} - 1 \right) \end{aligned} \quad (3.10)$$

The excess chemical potential  $\Delta\mu(Q)$  in (3.1) and the average interaction energy  $\langle U_{\text{elec}}(Q) \rangle$  in (3.7) represent the interaction of the charged solute with the charge density  $\rho_{\text{elec}}(r)$ ; e.g., for (3.1)

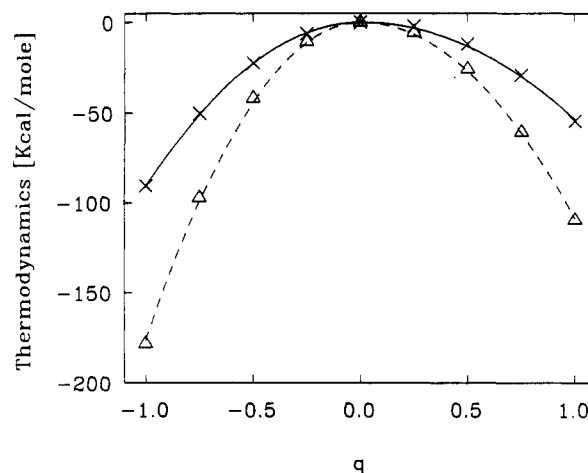
$$\Delta\mu(Q) = \int_0^Q dQ' \int d^3r \rho_{\text{elec}}(r;Q') \frac{1}{r} \quad (3.11)$$

If the density  $\rho_{\text{elec}}(r)$  is localized at the core boundary (i.e.,  $r \simeq \sigma$ ), the condition imposed by (3.10) leads to an essentially linear response of the solvent charge density around a charged solute, so that the excess free energy of charging,  $\Delta\mu(Q)$  in (3.1) and (3.11), is well approximated by the Born free energy for microscopic ions. This suggests that the failure of the Born model for highly charged ions arises from an improper choice of the ion radius.<sup>13,25</sup> It is the loss of ability of the nearby solvent molecules to reorient that leads to the change in the effective solute radius. This corresponds to a saturation of the dielectric response of the solvent in the vicinity of the ion and has been represented in terms of a distance-dependent dielectric constant  $\epsilon(r)$ .<sup>26</sup> Consequently, dielectric saturation and a charge-dependent Born radius are two manifestations of the same phenomenon on a microscopic level.

#### 4. RISM-HNC Calculation

In this section, we present results from a RISM calculation with the HNC closure for infinitely dilute ions in aqueous solution. The details of the calculations have been reported elsewhere;<sup>10</sup> the solvent used is a rigid three-site water model that is a slight variant of the TIPS3P potential<sup>27</sup> and the solutes are monatomic ions with their charge varying from  $-1$  to  $+1$  and Lennard-Jones parameters approximately equal to those for the chloride anion ( $\epsilon = 0.107$  kcal/mol,  $\sigma = 4.446$  Å).

In Figure 1 we show the dependence of the electrostatic part of the solvation free energy (3.1) and the average interaction energy (3.7) as a function of solute charge.<sup>10</sup> The symbols mark the solvation values calculated at  $Q = 0, \pm 0.25, \pm 0.5, \pm 0.75$ , and



**Figure 1.** Electrostatic components of solvation thermodynamics as a function of solute charge. ( $\times$ , —)  $\Delta\mu(Q)$ ; ( $\Delta$ , ---)  $\langle U(Q) \rangle$ . The four different branches were fitted to the quadratic expression  $-(\text{constant})Q^2$ , with the constant equal to 90.1, 53.3, 176.4, and 108.4 kcal/mol for  $\Delta\mu(-1)$ ,  $\Delta\mu(+1)$ ,  $\langle U(-1) \rangle$ , and  $\langle U(+1) \rangle$ , respectively.

**TABLE I: Position and Magnitude of the First Peak in the Solute-Solvent Radial Distribution Functions.**

$Q$	H		O	
	$r_{\text{max}}$ , Å	$g_{\text{max}}$	$r_{\text{max}}$ , Å	$g_{\text{max}}$
1.00	3.97	1.49	3.25	2.29
0.75	3.97	1.44	3.39	1.96
0.50	3.97	1.39	3.46	1.81
0.25	4.06	1.34	3.52	1.83
0.00	4.14	1.32	3.60	2.01
-0.25	4.14	1.33	3.60	2.24
-0.50	4.14 <sup>a</sup>	1.37	3.52	2.43
	2.10 <sup>b</sup>	0.88		
-0.75	2.05	2.12	3.52	2.59
-1.00	1.97	3.93	3.46	2.82

<sup>a</sup> The second peak in  $g(r)$ . <sup>b</sup> The first peak in  $g(r)$ .

$\pm 1$ . The lines are least-squared fits to them with quadratic functions of the solute charge. Thus, the full RISM-HNC solutions, as pointed out in the Introduction, lead to a  $Q^2$  dependence of the solvation thermodynamics, as expected from the Born equation. However, there is a significant difference between the free energy of positive and negative ions. This can be introduced as a difference between the values of  $\sigma$  for the two cases;<sup>8</sup> for the present calculations, the empirical fit gives  $\sigma_+ = 3.25$  Å and  $\sigma_- = 1.97$  Å.

Table I lists the positions ( $r_{\text{max}}$ ) and magnitudes ( $g_{\text{max}}$ ) of the first peaks in the radial distribution functions for the various charged solutes. Figures 2 and 3 present the correlation functions  $h(r)$  and  $c(r)$  for  $Q = \pm 1$ . The calculated  $c(r)$  (—) are compared with the approximate construction of (2.7) and (2.5) (---), where the  $\sigma$  is set equal to the position of the first peak in the radial distribution function. For the negative ion, the appropriate  $\sigma$  comes from the water hydrogen peak, while for the positive ion it comes from the water oxygen peak. For  $r > \sigma$ , the two curves are almost indistinguishable; the largest difference occurs for  $c(r)$  of oxygen-Cl<sup>-</sup> in Figure 2b. For  $r < \sigma$ , the agreement with (2.7) is not as good but it is satisfactory.

This comparison illustrates that our simple model contains the essential features of the solvation and that the numerical solutions of the RISM equation with the HNC closure and soft potentials retain much of the characteristics of the MSA closure. In the present calculations, however, the ionic radius  $\sigma$  results from a balance of interactions (soft core and electrostatics) and is an output of the numerical calculation; i.e., the position of the maximum,  $r_{\text{max}}$ , depends on the solute charge for soft-core potentials when solute and solvent are of similar sizes.

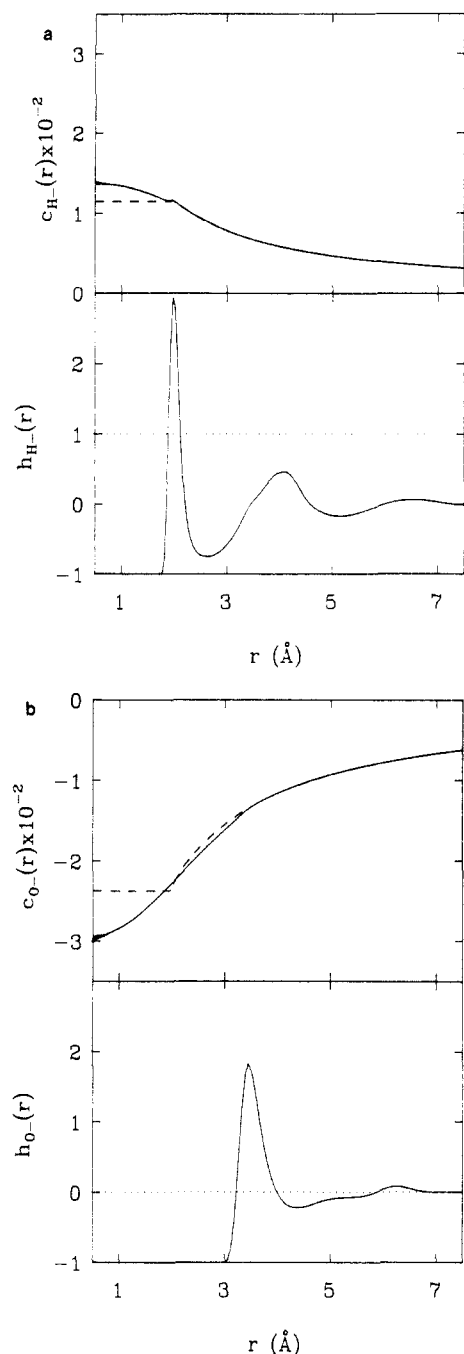
With the effective Born radius set equal to the position of the first peak, we compare the excess chemical potential as given by the exact expression (3.2) and the approximate expression for large

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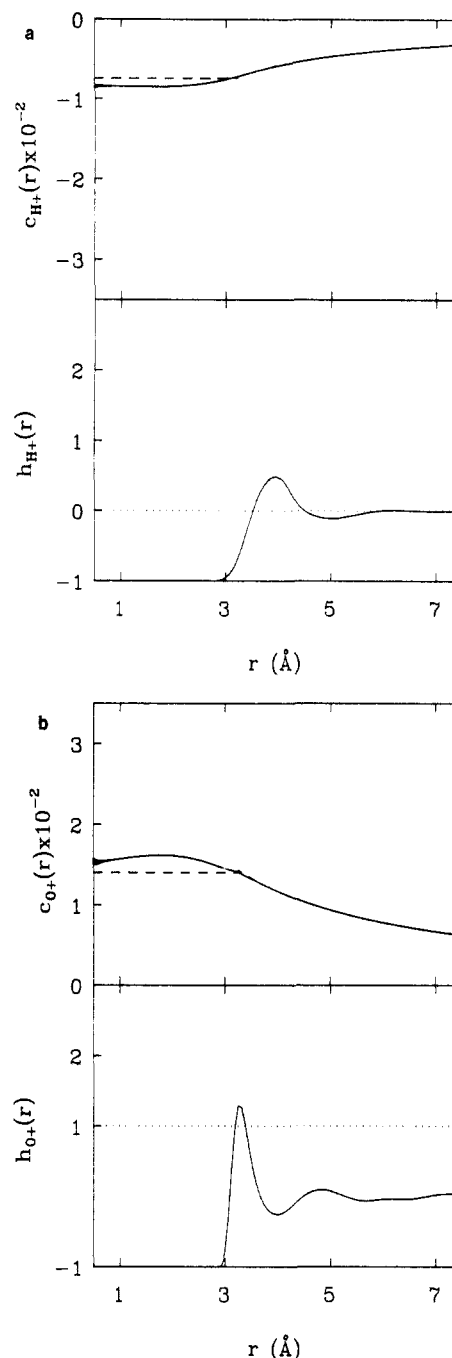
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**Figure 2.** Direct correlation function and the radial distribution functions for  $\text{Cl}^-$ . The approximate direct correlation functions using (2.7) and (2.5) are given as (---) lines. (a) Upper,  $c_{\text{H-Cl}^-}(r)$ ; lower,  $h_{\text{H-Cl}^-}(r)$ . (b) Upper,  $c_{\text{O-Cl}^-}(r)$ ; lower,  $h_{\text{O-Cl}^-}(r)$ .

solute (3.3). These results are given in parts a and b of Figure 4 for  $\text{Cl}^-$  and  $\text{Cl}^+$ , respectively, where we plot the integrand as a function of  $k$ . The major contribution to the electrostatic solvation free energy comes from  $k \leq \pi/\sigma$  where the two curves agree well with each other. The approximate integral of (3.3) leads to  $-80$  and  $-49$  kcal/mol compared with  $-90$  and  $-54$  from (3.2) for  $\text{Cl}^-$  and  $\text{Cl}^+$ , respectively. The discrepancy arises from the fact that a significant fraction of the chemical potential comes from contributions located between the core region ( $h(r) = -1$ ) and the first peak position in  $h(r)$ , introducing some uncertainty in the choice of the best  $\sigma$ . Use of a slightly smaller radius would give better numerical agreement and not be inconsistent with the asymptotic analysis. Alternatively, the Born radius can be determined from the first peak in the integrand of (3.1); i.e.

$$\sigma \approx \text{MAX} \left[ \sum_{\gamma} h_{\gamma}(r; Q) \rho q_{\gamma} \frac{Q}{r} \right] \quad (4.1)$$



**Figure 3.** Direct correlation function and the radial distribution functions for  $\text{Cl}^+$ . The approximate direct correlation functions using (2.7) and (2.5) are given as (---) lines. (a) Upper,  $c_{\text{H-Cl}^+}(r)$ ; lower,  $h_{\text{H-Cl}^+}(r)$ . (b) Upper,  $c_{\text{O-Cl}^+}(r)$ ; lower,  $h_{\text{O-Cl}^+}(r)$ .

The factor of  $1/r$  in (4.1) decreases the Born radius relative to the peak in the radial distribution function and agrees better with the exact calculations. However, use of the peak itself gives a ratio  $r_{\text{max}}^{(+)} / r_{\text{max}}^{(-)} = 1.67$  for the positive and negative ions in excellent agreement with the ratio of their chemical potential  $\Delta\mu^{(-)} / \Delta\mu^{(+)} = 1.63$ . This result provides strong support for the empirical rule of Latimer et al.<sup>8</sup> In the limit of a very large spherical solute, the Born radius is insensitive to the sign of the ion charge. For water "large" means that the first peak in the solute-solvent radial distribution function is located at a distance much larger than the distance (0.59 Å) between the oxygen and the point located between the two hydrogens. In empirical energy functions, the interaction sites need not coincide with actual massive particles, such as in the TIP4P<sup>27</sup> or the ST2<sup>28</sup> water models. In those cases, the expression given by (4.1), where the summation includes all

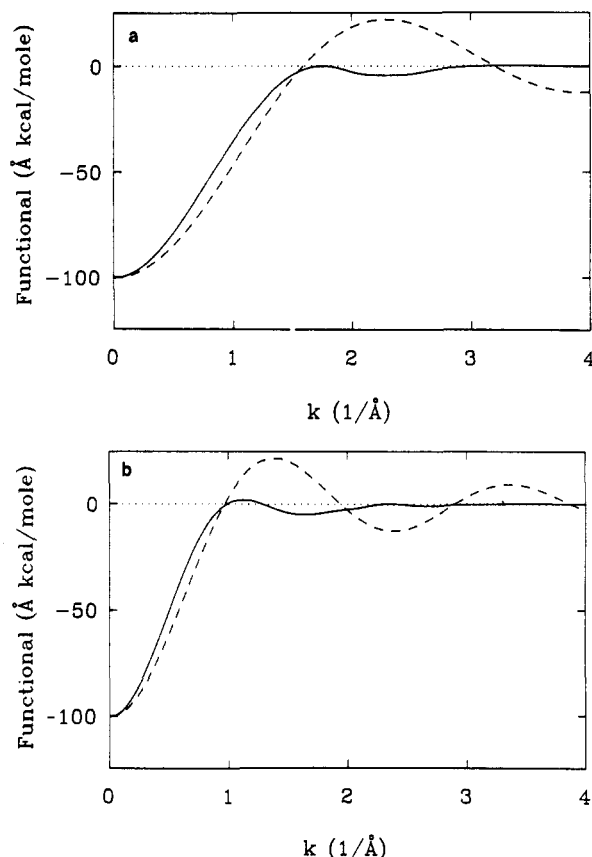


Figure 4. Electrostatic free energy functional in  $k$  space. (—) (3.2); (---) (3.3). (a)  $\text{Cl}^-$ ; (b)  $\text{Cl}^+$ .

interaction sites, represents a more consistent and general criterion for defining a Born radius. For a fully charged solute, the sum is often dominated by one ion-site distribution function and the simpler rule may be used.

### 5. Macroscopic Model

A connection between the statistical mechanical analysis and the phenomenology of macroscopic electrostatics can be made. The analogue of the charging formula for a linear dielectric is<sup>29</sup>

$$\Delta\mu = \frac{1}{4\pi} \int_0^D \int d^3r \Delta\vec{E} \cdot \delta\vec{D} \quad (5.1)$$

where  $\vec{D}$  is the electric displacement vector and  $\Delta\vec{E}$  is the excess electric field after the reference vacuum contribution has been removed

$$\Delta\vec{E} = \vec{E}_{\text{solvent}} - \vec{E}_{\text{vacuum}} \quad (5.2)$$

Integrating by parts once leads to a surface integral at the solute-solvent interface

$$\Delta\mu = \frac{1}{4\pi} \int_0^Q dQ' \int d^2s (\Delta\vec{E} \cdot \hat{n}) \frac{1}{r} \quad (5.3)$$

where  $\hat{n}$  is the outward normal to the surface at  $|\mathbf{r}| = \sigma$ . The integral can be rewritten in terms of a volume integral by inserting a  $\delta$  function in the integrand. We obtain

$$\begin{aligned} \Delta\mu &= \int_0^Q dQ' \int d^3r \left( \Delta\vec{E} \cdot \hat{n} \frac{\delta(|\mathbf{r}| - \sigma)}{4\pi} \right) \frac{1}{r} \\ &= \int_0^Q dQ' \int d^3r \left( \frac{1}{\epsilon} - 1 \right) Q' \frac{\delta(|\mathbf{r}| - \sigma)}{4\pi\sigma^2} \frac{1}{r} \end{aligned} \quad (5.4)$$

This expression can be compared with (3.1) and (3.11). In the continuum limit, the electric charge density due to the solvent

$$\rho_{\text{elec}}(\mathbf{r}; Q) = Q \left( \frac{1}{\epsilon} - 1 \right) \frac{\delta(|\mathbf{r}| - \sigma)}{4\pi\sigma^2} \quad (5.5)$$

is "concentrated" at the solute-solvent interface,<sup>30</sup> in accord with a hard-sphere or  $\delta$ -function approximation. In the microscopic description the surface has a thickness comparable to the width in the first peak of the radial distribution function as shown by (3.9).

### 6. Concluding Discussion

The continuum limit of the RISM integral equation in its extended form has been shown to be consistent with the Born model of solvation. This is seen to be a consequence of the asymptotic properties of the solute-solvent direct correlation function, which have the correct form within the RISM-HNC approximation,<sup>24</sup> although the dielectric constant needs to be adjusted empirically to the experimental value. The agreement increases our confidence both in the phenomenological Born model and in the RISM integral equation for calculating excess free energy of solvation for complex molecular systems. Although the RISM integral equation does not follow from a rigorous statistical mechanical treatment of molecular fluids,<sup>31</sup> it has been shown to reproduce many of the features obtained from simulations of ionic solutions.<sup>27,32,33</sup> The fundamental justification of the Born equation for a realistic solvent model supports its utility for the study of ion solvation. However, a direct comparison with experimental values of  $\Delta\mu$  should be done with caution since the Born expression includes only the electrostatic contribution to the chemical potential, i.e., the free energy of charging a neutral sphere in a polar solvent. The free energy of the neutral sphere itself must be included in the free energy before it can be compared with experiments by a precise procedure. For ions, RISM-HNC equation estimates<sup>10,34</sup> indicate that the "cavity" contribution is of the order of 10% of the Born free energy of charging. A "neutral" chloride is found to have a chemical potential of +12 kcal/mol and the electrostatic contribution is -90 kcal/mol, which yields a total chemical potential of -78 kcal/mol. A "neutral" potassium has a chemical potential of +6 kcal/mol and the electrostatic contribution is -69 kcal/mol, which corresponds to a total chemical potential of -63 kcal/mol. Thus, use of the Born model to determine solvation free energies corresponds to an empirical rescaling of the Born radius to incorporate this contribution.<sup>4</sup>

While the Born model provides a good estimate of the excess chemical potential of ions, it does not yield a useful route to determine the enthalpy and entropy of solvation. The thermodynamic relation

$$\Delta h = \Delta\mu + T \left( \frac{\partial \Delta\mu}{\partial T} \right) \quad (6.1)$$

must be used with extreme caution in the context of the Born model because of the sensitivity of the Born radius to the temperature. As an illustration we consider the case of  $\text{Cl}^-$ . From the Born free energy (3.6) and (6.1), the enthalpy of solvation is

$$\Delta h = \Delta\mu \left[ 1 + \frac{T}{(\epsilon - 1)\epsilon} \left( \frac{\partial \epsilon}{\partial T} \right) - \frac{T}{\sigma} \left( \frac{\partial \sigma}{\partial T} \right) \right] \quad (6.2)$$

Applying this expression to the case of  $\text{Cl}^-$ , we find that the variation of the dielectric constant with respect to the temperature contributes only -1.8% to the enthalpy of solvation. In RISM integral calculations<sup>10,35</sup> as well as in experiments,<sup>36,37</sup>  $\Delta h$  is found

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to be 10–20% larger in magnitude than  $\Delta\mu$ . Thus, the variation of  $\epsilon$  with temperature is not sufficient to account for the observed difference between  $\Delta h$  and  $\Delta\mu$ . The dominant contribution to this difference arises from the variation of the Born radius with temperature, which has been neglected in ref 4 and in subsequent work.<sup>5</sup> In the case of  $\text{Cl}^-$ , a value of  $\partial\sigma/\partial T = -8.4 \times 10^{-4} \text{ Å/K}$  was obtained from the RISM temperature derivative<sup>10,35</sup> and it leads to 12.7% increase of the enthalpy over the free energy. Thus, unless a very precise procedure for evaluating the dependence of the radius on the temperature is available, the Born model should be restricted to the chemical potential  $\Delta\mu$ .

The analysis of this paper is based on the observations (i) that the asymptotic behavior of the direct correlation function  $c_a(r)$  (2.3) and the existence of a core condition for  $h_a(r)$  (2.4) are generally valid; (ii) a MSA-like extension of  $c_a(r)$  by (2.4) down to ranges the size of a typical solute repulsive core; and (iii) the assumption that the effective Born radius in (1.1) is independent of the solute charge for large solute. Conditions (i)–(iii) are satisfied in earlier studies where the MSA closure for hard-sphere ion dissolved in dipolar hard-sphere solvent gave an exact  $Q^2$  dependence.<sup>7,38</sup> From our extension to soft-core systems with the RISM-HNC calculations (i) and (ii) are the essential requirement; Born model solvation behavior is still obtained when the solute and the solvent are of similar size if condition (iii) is relaxed.

Our analysis enables us to identify the effective Born radius for charged solute with realistic soft-core potential as the distance  $r$  at which the function  $[\rho_{\text{elec}}(r;Q)Q/r]$  is a maximum. For ions, this is seen to correspond to the first peak in the solute–solvent radial distribution function. The Born radius is, thus, found to be a function of the sign of the solute charge and to reflect the fact that the dipolar water molecule reorients itself differently in the presence of an anion or a cation. The off-center hydrogen site in the water invariably leads to an effective Born radius for the anion smaller than the cation if the two ions have the same Lennard-Jones radius. This observation is in agreement with the

calculations of Hirata et al.<sup>23</sup> and is also consistent with the suggestion made by Rashin and Honig<sup>4</sup> that the Born radius corresponds to the size of the cavity formed by an ion in a particular solvent; e.g., they found a radius of 1.94 Å for  $\text{Cl}^-$ , in good agreement with the present analysis. However, the radius of 2.17 Å for  $\text{K}^+$ , chosen to agree with an enthalpy of solvation  $\Delta h$  of  $-76.8 \text{ kcal/mol}$ ,<sup>4</sup> is smaller than the expected value. A radius of 2.6 Å is in accord with the RISM-HNC radial distribution function and electrostatic solvation free energy. Thus, there appears to be an inconsistency between the positive and negative ion results. The smaller radius may be due in part to the fact that the variation of the Born radius with respect to temperature in the enthalpy was neglected in the empirical fitting procedure (see above). However, there is the possibility that the discrepancy arises also from an intrinsic deficiency of the water interaction potential, represented here by a three-site model. The presence of “lone pairs”, such as in the ST2 model,<sup>28</sup> would decrease the effective Born radius of a positive ion by bringing the interaction sites closer to the positive ion; e.g., for the ST2 water model, the “lone-pair” sites are  $\approx 0.5 \text{ Å}$  closer to an ion than the oxygen interaction site. Preliminary results obtained from Monte Carlo simulations indicate that the second solvation shell make a significant contribution to the solvation free energy for a small ion. As the radius of an ion becomes larger, the Born-like asymptotic behavior dominates the solvation free energy and these deviations become small, as described above.

In the infinite dilution limit the solvent density correlation function  $\chi_{vv}$  is an input in the theory. The present calculation used an RISM-HNC pure water radial distribution function. Improvement can be achieved by modifying the density correlation function to yield accurate long- and short-wavelength properties as well as by using more accurate site–site solute–solvent closure.<sup>18,22,35</sup>

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## Alkyl Chains in a Nematic Field. 1. A Treatment of Conformer Shape

Demetri J. Photinos,<sup>†</sup> Edward T. Samulski,\* and Hirokazu Toriumi<sup>‡</sup>

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

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A theory is presented for the explicit inclusion of molecular shape anisotropy and flexibility in the description of the interactions associated with alkyl chains in the nematic phase. This description yields quantitative agreement with observed deuterium quadrupolar and dipolar NMR splittings, using the conventional parameters of the rotational isomeric state model for the chain. Orientational correlations between neighboring chain segments are introduced to distinguish conformations which are energetically indistinguishable in previous single segment interaction models. A detailed analysis of the deuterium NMR observations on decane- $d_{22}$  dissolved in a nematic solvent is presented. The new approach gives clear insights into the relevant aspects of flexible molecules experiencing a uniaxial constraint and enables us to understand the shortcomings of previous efforts to model flexible molecules in the nematic phase.

### I. Introduction

Alkyl chains, an essential component of thermotropic liquid crystals, were explicitly incorporated into molecular theories of mesophase formation in 1974 when Marcelja<sup>1</sup> extended the

Maier–Saupe<sup>2</sup> (M–S) theory of the thermally induced nematic–isotropic transition. The molecular origins of the Maier–Saupe mean field were attributed to anisotropic dispersion forces, although it has been subsequently recognized that the form of the mean field equations may be derived from different origins, e.g., pure excluded volume interactions.<sup>3,4</sup> Independent of the mo-

\* Address correspondence to this author.

<sup>†</sup> Permanent address: Department of Physics, University of Patras, Patras 26110, Greece.

<sup>‡</sup> Permanent address: Department of Chemistry, University of Tokyo, Komaba, Tokyo 153, Japan.

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