

Ionic Solution Theory for Non-ideal Solvents

Potential of Mean Force between Ions

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A comparison is made between fully microscopic models of an ionic solution in a dipolar solvent, in which the solvent as well as the solute is treated on a molecular basis, and quasimacroscopic models, in which the solvent is treated as an ideal continuum. The central objects of inquiry are the molecular potentials of mean force, especially the ion-ion potential in the limit of infinite solute dilution.

Our aim here will be to discuss certain features of ion-ion and ion-solvent interaction from the point of view of statistical mechanics, which serves as a bridge between the microscopic and macroscopic descriptions of a system; that is to say, between its molecular and continuum descriptions. In an ionic solution, the primary elements of this bridge are the set of n -particle probability distribution functions $g_n(1, \dots, n)$ that measure the probability of finding n particles in the system in a given configuration, or, equivalently, the associated potentials of mean force $W_n(1, \dots, n)$, where $-\beta W_n(1, \dots, n) = \ln g_n(1, \dots, n)$, with β^{-1} equal to Boltzmann's constant k times absolute temperature T . Of the g_n , the radial distribution function $g_2(1, 2) = \exp -\beta W_2(1, 2)$ embodies the most important features of molecular structure, and it is $W_2(1, 2)$ that will be our chief focal point.

The molecular model with which we shall be concerned here is a classical non-relativistic one, defined by a potential energy between n particles, $\varphi_n(1, \dots, n)$ which is the pairwise additive sum of two-body terms $\varphi_2(1, 2)$, $\varphi_n(1, \dots, n) = \sum_{1 \leq i < j \leq n} \varphi_2(i, j)$.

We treat the whole system, including solvent as well as ions, on a molecular level,* so that we have a solvent-solvent interaction $\varphi_{VV}(1, 2)$ and solute-solvent interaction $\varphi_{UV}(1, 2)$ as well as a solute-solute interaction $\varphi_{UU}(1, 2)$ between ions to consider. We shall assume that all of these interactions have a repulsive core that becomes infinite (say, faster than $1/r^6$) as r , the distance between particle centres, goes to zero. We shall further assume (as appropriate in considering ions in dipolar solvents) that as $r \rightarrow \infty$, $\varphi_{UU}(1, 2)$ is dominated by the Coulombic interaction between point charges of magnitude q_1 and q_2 , $\varphi_{UV}(1, 2)$ by the ideal charge-dipole interaction between a

* It is in this sense that we use the term "non-ideal solvent" in our title, to distinguish our underlying Hamiltonian model from models in which the solvent is treated as an ideal continuum from the start.

point charge of magnitude q_1 and a dipole of moment μ_2 , and $\phi_{VV}(1, 2)$ by the ideal dipole-dipole interaction between dipoles of moment μ_1 and μ_2 .

The macroscopic *continuum* associated with the above model is simply the fluid of particles as described above, viewed by an observer who becomes infinitely large relative to the radii b_U and b_V of the solute and solvent particles, respectively. For the fluid in equilibrium, the exact continuum description is thus just the thermodynamic description in the usual thermodynamic (*i.e.*, infinite-system) limit.

In addition to the wholly homogeneous macroscopic continuum with which the above limit coincides, there is a more complicated macroscopic configuration that will also prove important to us—a collection of i spherical domains or macroparticles of dielectric constant ϵ_0 and radius b_i in a continuum of dielectric constant ϵ . At the centre of each domain is a point charge of magnitude q or an ideal dipole of moment μ . The full electrostatic potential of interaction between a pair of such domains includes all induced domain-solvent contributions, and is too complicated a function to be represented in simple closed form, but its dominant large- r properties are easily given.¹⁻³ For example (setting $\epsilon_0 = 1$ for simplicity) in the case of two charged domains whose centres are a distance r apart, one has as $r \rightarrow \infty$,

$$W_{qq}(1, 2) \rightarrow \frac{q_1 q_2}{r\epsilon} + \frac{\epsilon - 1}{2r^4(2\epsilon + 1)\epsilon} (q_1^2 b_2^3 + q_2^2 b_1^3) + \dots, \quad (1)$$

where we use W with subscripts q (for charges) and d (for dipoles) to denote the domain-domain potentials. As $r \rightarrow \infty$, the ratio of the $W_{qq}(1, 2)$ to the ideal charge-charge pair potential $\phi_{qq}(1, 2)$ is thus a direct measure of the dielectric constant of the continuum in which the spherical domains are immersed:

$$W_{qq}(1, 2)/\phi_{qq}(1, 2) \xrightarrow{r \rightarrow \infty} \frac{1}{\epsilon}. \quad (2a)$$

Similarly,³ the ratio of charged-domain, dipolar-domain interaction to the ideal charge-dipole potential $\phi_{qd}(1, 2)$ goes to $3/(2\epsilon + 1)$ (which we write as $(1/\epsilon)[3\epsilon/(2\epsilon + 1)]$ for reasons that will be immediately clear),

$$W_{qd}(1, 2)/\phi_{qd}(1, 2) \xrightarrow{r \rightarrow \infty} \frac{1}{\epsilon} \left(\frac{3\epsilon}{2\epsilon + 1} \right), \quad (2b)$$

while for the dipole-dipole case we have

$$W_{dd}(1, 2)/\phi_{dd}(1, 2) \xrightarrow{r \rightarrow \infty} \frac{1}{\epsilon} \left(\frac{3\epsilon}{2\epsilon + 1} \right)^2. \quad (2c)$$

One might intuitively expect that the microscopic $W_{UU}(1, 2)$ will behave, in the limit of vanishingly small ion concentration, much like the macroscopic $W_{qq}(1, 2)$ of eqn (1). To the extent that this expectation is realized—and we shall discuss below its statistical mechanical status—one will find useful a quasi-continuum model of an ionic solution in which the solvent is regarded as a continuum of dielectric constant ϵ but the ions retain their status as particles, with the infinite-dilution $W_{UU}(1, 2)$ prescribed so as to conform to eqn (1) for large r and satisfactorily mirror the presence of a highly repulsive interaction core as $r \rightarrow 0$. In perhaps the simplest version of such a model, one regards the ions as elastic spheres of dielectric constant unity into which point charges have been centrally embedded, so that the ion-ion potential of mean force at zero ion concentration is given by

$$\begin{aligned} W_{UU}^0(1, 2) &= \infty \text{ for } r < b_1 + b_2 \\ W_{UU}^0(1, 2) &= W_{qq}(1, 2) \text{ for } r > b_1 + b_2 \end{aligned} \quad (3)$$

where b_i is the radius of ion i , and the superscript zero here and below refers to the infinite-dilution limit of ion concentration.

Although the kind of quasi-continuum picture that leads to eqn (3) has clearly lain behind much of the conceptual development of ionic solution theory, as well as that of the closely related theory of the dielectric properties of polarizable and polar fluids,¹ the explicit computational use of $W_{\text{qq}}(1, 2)$ as the large- r form of $W_{\text{uu}}^0(1, 2)$ has not been widespread in theoretical studies of ionic solutions. Levine and his coworkers have been exploiting it for some time,^{2,4} but it has only been systematically incorporated into the functional form of an approximate $W_{\text{uu}}^0(1, 2)$ to be used in statistical-mechanical computations (via the "refined model" of Friedman and his group)⁵ in the 1970's. The main obstacle to its earlier use does not seem to have been diffidence over its conceptual status, but rather the fact that $W_{\text{qq}}(1, 2)$ is itself not representable in simple closed form, plus the fact that until very recently even the crudest tenable approximation, far cruder than that given by eqn (3), has already represented a formidable statistical mechanical challenge of compelling interest and importance when used as input in McMillan-Mayer theory. This approximation (explicitly introduced by Mayer⁶ in 1950 although implicit in a great deal of earlier work) is given by

$$\begin{aligned} W_{\text{uu}}^0(1, 2) &= \infty \text{ for } r < b_1 + b_2 \\ W_{\text{uu}}^0(1, 2) &= q_1 q_2 / \epsilon r \text{ for } r > b_1 + b_2, \end{aligned} \quad (4a)$$

which is usually taken together with the assumption that the n -(solute) particle potentials of mean force at zero solute concentration are pairwise additive,

$$W_{\text{u}}^0 \dots \text{u}(1, \dots, n) = \sum_{1 \leq i < j \leq n} W_{\text{uu}}^0(i, j). \quad (4b)$$

The analytic approximation of the structure [e.g., of $W_{\text{uu}}(1, 2)$ at arbitrary ion concentration] and osmotic thermodynamics of a system of ions with the $W_{\text{u}}^0 \dots \text{u}$ given by eqn (4) is only just now becoming a high-precision enterprise, and that in itself is an important piece of news that we want to broadcast here. For ions of equal radii, we now have nearly exact analytic* approximation procedures for the 1-1 electrolyte regime which remain reasonably accurate throughout the 2-2 regime as well.⁷ For the unequal-diameter case things are in much less well-developed shape, but the groundwork has been laid; accurate analytic approximations for the osmotic thermodynamics are already in a reasonably advanced state of development⁸ and good approximations for $W_{\text{uu}}(1, 2)$ itself can be expected to follow within the next couple of years or so. (There are two promising competing approaches to the unequal-diameter case. One is *via* the solution of the mean-spherical approximation for that case.⁸ The other is *via* the use of thermodynamic perturbation theory and its variants,⁹ using an equal-diameter reference system.) We must refrain from further discussion of these major quantitative advances, however, if we are to touch at all upon the fascinating question of the *conceptual* relationships among eqn (2), (3) and (4), to which we now turn.

First of all, one can ask in what sense, if any, eqn (4) corresponds to a *bona-fide* Hamiltonian model, and how that model differs from that associated with eqn (3). On a macroscopic scale, the status of eqn (4) was elucidated by Friedman¹⁰ (who introduced the term *primitive model* to describe that equation). He observed that the equation precisely characterizes the W_{qq} to be expected in the macroscopic-continuum

* By analytic, we mean susceptible to closed-form representation or involving, at worst, simple quadratures and transcendental equations. Highly accurate integral-equation results, such as those of the HNC approximation, have been already available from Rasaiah and Friedman for over a decade, but these are not analytic in our sense.

model which we discussed above eqn (1), as long as ε_0 is set equal to ε instead of 1, and the spherical macro-domains are imagined as having infinitely repulsive rigid walls when interacting with one another. A question left open by this observation is what microscopic Hamiltonian can give rise to such a macroscopic model, and this was subsequently investigated by one of us.¹¹ The limiting process we considered rests upon the observation that the macroparticles described by both eqn (3) and (4) can be thought of as being perfectly impermeable to one another, differing only in their permeability to the solvent, with the particles described by eqn (3) perfectly impermeable to the solvent (and hence empty of solvent) but the particles described by eqn (4) completely permeable to the solvent (and hence filled with it). It is natural to describe this selective permeability in terms of core potentials with non-additive diameters, as one considers the limit in which the ions become infinite in size compared with the solvent particles, and it is so described in ref. (11).

To assess the validity of approximations like eqn (3) and to improve upon them, we must understand how the ratios given in eqn (2) compare with the corresponding microscopic ratios $W_{UU}^0(1, 2)/\phi_{UU}(1, 2)$, $W_{UV}^0(1, 2)/\phi_{UV}(1, 2)$ and $W_{VV}^0(1, 2)/\phi_{VV}(1, 2)$ computed from the molecular model. The comparison was first contemplated by Jepsen and Friedman.³ They noted that for $r \rightarrow \infty$ the two sets of ratios should become asymptotically identical in a limit in which the charge and dipole strengths become infinitely weak [*i.e.*, $\beta\phi(1, 2) \rightarrow 0$] and the ions infinitely large compared with the solvent particles (*i.e.*, $b_v/b_u \rightarrow 0$). A separate but closely related question is how the two sets of ratios will compare for $r \rightarrow \infty$ if one does *not* take the weak-strength, large-ion limits. There is nothing written in the sky that says they should be the same, and Jepsen and Friedman³ found that beyond the lowest order in $y = \frac{4\pi}{9} \beta\mu^2\rho$ they appeared to be different in the low-density approximation they were considering. Nienhuis and Deutch¹² have more recently argued that the result to be expected, to all orders in density, is

$$W_{UU}^0(1, 2)/\phi_{UU}(1, 2) \xrightarrow{r \rightarrow \infty} \frac{1}{\varepsilon}, \quad (5a)$$

as in the macroscopic case given by eqn (2a), but in contrast to eqn (2b) and (2c),

$$W_{UV}^0(1, 2)/\phi_{UV}(1, 2) \xrightarrow{r \rightarrow \infty} \frac{1}{\varepsilon} \left(\frac{\varepsilon - 1}{3y} \right) \quad (5b)$$

and

$$W_{VV}^0(1, 2)/\phi_{VV}(1, 2) \xrightarrow{r \rightarrow \infty} \frac{1}{\varepsilon} \left(\frac{\varepsilon - 1}{3y} \right)^2. \quad (5c)$$

We have confirmed¹³ these results by means of a derivation which is formally exact (thus obviating certain assumptions made by Nienhuis and Deutch). Our treatment^{13,14} further explicates the Jepsen–Friedman results in the following way: we note that the results of eqn (2) and (5) coincide if and only if ε is given by the Onsager expression¹⁵

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = y. \quad (6)$$

This is consistent with the result given in ref. (14) that only in the *Onsager-continuum limit*, in which eqn (6) becomes exact, is the dielectric response to each solvent dipole that of a vacuum in a macroscopic sphere surrounding the solvent dipole. Thus, only in the Onsager continuum limit are the assumptions satisfied under which one can

identify each solvent particle as a macrosphere within which $\varepsilon = 1$, and so assure the identity of the full set of ratios in eqn (2) and (5).

As yet, we have considered $W_2(1, 2)$ here only in the zero ion-concentration limit. As soon as the concentration is non-zero, profound changes in the large- r form of the $W_2(1, 2)$ can be anticipated. Although it is widely assumed that $W_{UU}(1, 2)$ has the form*

$$W_{UU}(1, 2) \xrightarrow{r \rightarrow \infty} A_{UU} q_1 q_2 e^{-\lambda r / r \varepsilon}. \quad (7)$$

Stillinger and White¹⁶ have strikingly demonstrated that even this seemingly reasonable assumption should not be taken for granted, by showing how other seemingly reasonable assumptions lead instead to the conclusion that $W_{UU}^0(1, 2) \rightarrow O(r^{-8})$ as $r \rightarrow \infty$!

On the other hand, in as yet unpublished studies Groeneveld and the authors have demonstrated that assuming the convergence, or at least the asymptotic relevance, of certain cluster expansions for the direct correlation function, eqn (7) follows in the primitive model, and we have found no reason to doubt that it is also the limiting form for $W_{UU}(r)$ when the solvent is treated as a molecular fluid rather than a continuum. However, one clearly *cannot* in general expect the λ in eqn (7) to be the Debye-Hückel inverse correlation length $\kappa = (4\pi\beta\rho e^2)^{1/2}$, with ρ = total ionic number density, or the factor A_{UU} to be unity [see eqn (9) below, for example].

When the ionic concentration ρ is not vanishingly small, one expects W_{UV} and W_{VV} as well as W_{UU} to be exponentially shielded. The first detailed evidence for this emerged from a monumental analysis of the mean spherical approximation by Adelman and Deutch,¹⁷ who discovered such shielding by scrutinizing the Laplace transforms of W_{UV} and W_{VV} in that approximation applied to a system of charged-sphere ions in a dipolar-sphere solvent, with charge-dipole solute-solvent interactions present. We have recently¹⁸ made a study of the exact large- r form of W_{UV} and W_{VV} as well as W_{UU} for a symmetric electrolyte in the low q (or low ρ) regime and find, as $r \rightarrow \infty$,

$$W_{UU}/\phi_{UU} \rightarrow \frac{1}{\varepsilon} e^{-\lambda r} \quad (8a)$$

$$W_{UV}/\phi_{UV} \rightarrow \frac{\varepsilon - 1}{3y} \frac{1}{\varepsilon} (1 + \lambda r) e^{-\lambda r} \quad (8b)$$

$$W_{VV}/\phi_{VV} \rightarrow \left(\frac{\varepsilon - 1}{3y}\right)^2 \frac{1}{\varepsilon} (1 + \lambda r + \frac{1}{3}\lambda^2 r^2) e^{-\lambda r}. \quad (8c)$$

For low q or low ρ ,

$$\lambda = \varepsilon^{-1/2} \kappa, \quad (9)$$

but eqn (8) may well prove to have a much larger domain of validity than eqn (9). These results are fully consistent with the conclusions of Adelman and Deutch, and in addition reveal the presence of remarkable polynomial factors in W_{UV} and W_{VV} , along with the expected prefactors which survive in the zero ion-concentration limit to yield eqn (5).

There seems to be little hope of exactly characterizing the A_{UU} or λ of eqn (7) in simple thermodynamic terms except in certain limits such as that yielding eqn (9). In

* Here and for the rest of our discussion, we have in mind only the case of model potentials ϕ_{UU} , ϕ_{UV} and ϕ_{VV} in which there are no inverse-power terms beyond ϕ_{qq} , ϕ_{qd} , and ϕ_{dd} , respectively. Any r^{-p} terms in the ϕ values will in general give rise to such terms in the corresponding W values.

contrast, for ions of one sign in a neutralizing continuum solvent of dielectric constant ϵ , we have given¹⁹ the exact results $(\kappa/\lambda)^2 = \beta(\partial P/\partial \rho)_\beta$, $A_{UU} = (\lambda/\kappa)^4$.

Stillinger and Lovett have shown²⁰ that their second-moment condition on $g_{UU} = \exp -\beta W_{UU}$ can be expected to apply to molecular-solvent as well as continuum-solvent models, while we¹⁹ have extended the application of that condition to g_{VV} in the absence of ions, to yield a new expression for the ϵ of a polar fluid.

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