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Self-consistent-field treatment of the dissociation of bound molecules in solution

Carlos E. Galindo and J. B. Sokoloff
Physics Department, Northeastern University, Boston, Massachusetts 02115

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We present calculations of the dissociation of hydrogen-bonded molecules in solution, using a mean-field theory based on a variational method [N.R. Werthamer, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, New York, 1976), Vol. I, Chap. V]. The solvent is accounted for by a dielectric constant, and the effect of salt ions in solution on hydrogen bonding is treated by means of Soumpasis's potential of mean force [D. M. Soumpasis, Proc. Natl. Acad. Sci. USA **81**, 5116 (1984)]. At high concentrations, the effect of salt ions on the interaction is dominated by an effective temperature-dependent interaction, which results from a position-dependent term in the entropy resulting from the hard-core volume exclusion. In addition to describing the dissociation transition, this procedure provides the temperature and electrolyte-concentration dependence of the vibrational spectrum. The sample calculation by Gao and Prohofsky [J. Chem. Phys. **80**, 2242 (1984)] of two ammonia molecules bound together by a hydrogen bond in a vacuum is reconsidered in an ionic solution. Our method is also applied to the treatment of the hydrogen-bond dissociation of a pair of water molecules and of a hydrogen-bonded pair of negative point-charge ions. The latter is intended as a simple model for the dissociation of a single hydrogen-bonded base-pair unit of a DNA double helix.

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I. INTRODUCTION

Most processes of biological interest involve weakly associated molecules. Hydrogen-bonded complexes and ions in an aqueous solution constitute important examples. Typical bond energies are of the order of 0.13 eV per molecule (3 kcal/mol). The intermolecular forces responsible for the formation and stability of these systems are dominated by two features. These are the Coulomb interactions between charges or multipoles and the steric constraints characterized by a strong repulsion at short distances due to the overlap of the electronic shells. The mean-field approximation is a way to treat a large set of interacting molecules, by studying a typical molecule in an average field due to all the other molecules which must be determined self-consistently. In this paper we will apply this average field, or the potential of mean force (PMF) to describe the dissociation of a pair of molecules. The program will be as follows. Section II is a brief review of the variational method used in this work [1–3]. Section III is an account of the role of the PMF in describing the interaction of two particular ions or molecules. Section IV is intended to describe in more detail a term in the free energy due to the hard-core exclusion that leads to an effective attractive interaction. In Sec. V we apply the method to three hydrogen-bonded systems, two hydrogen-bonded negative ions (anions), two ammonia, and two water molecules. Section VI is a discussion of the results.

II. A SELF-CONSISTENT MEAN-FIELD THEORY

In this mean-field theory, a variational harmonic Hamiltonian with force constant ϕ is used in the quantum-statistical-mechanical variational principle. The variational free energy is minimized and the values of the force constant are determined for a temperature T. This method was called the self-consistent phonon approximation because it was originally used to calculate large-amplitude phonons in a crystal lattice (e.g., at high temperatures or for quantum solids which have a good deal of zero-point motion) [3], but being simply a variational method with a harmonic variational Hamiltonian, it can equally well be applied to two molecules interacting with an effective potential of mean force, as considered in this work. The method is able to approximately treat *anharmonic effects.* The Hamiltonian is

$$H=E_k+V(\mathbf{r}_1,\mathbf{r}_2;\{\alpha\})\ ,$$

where E_k is the kinetic energy and $V(\mathbf{r}_1,\mathbf{r}_2;\{\alpha\})$ is the potential energy of interaction. The last term depends on the separation between the centers of the two molecules located at $\mathbf{r}_1$ and $\mathbf{r}_2$ which is equal to $|\mathbf{r}_2-\mathbf{r}_1|$, and $\{\alpha\}$ is a set of parameters fixing the relative orientation of the molecules as well as contributions from the electric moments and polarizabilities. The free energy is

$$F=-k_BT\ln\mathrm{Tr}[\exp(-H/k_BT)]\ .$$

The variational Hamiltonian is

$$H_0=E_k+\tfrac{1}{2}\phi u^2\ ,$$

where ϕ is the variational force constant and u the displacement from the equilibrium position R, i.e., $|\mathbf{r}_2-\mathbf{r}_1|=R+u$. This expression has the form of a harmonic Hamiltonian but it is important to note that this variational method can treat *large displacements* due to the self-consistency. The variational free energy is given by

$$F_1\equiv F_0+\langle H-H_0\rangle_0\ ,$$

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where

$$F_0=-k_BT\ln\mathrm{Tr}[\exp(-H_0/k_BT)]\ ,$$

and we use the notation

$$\langle\theta\rangle_0\equiv\frac{\mathrm{Tr}[\theta\exp(-H_0/k_BT)]}{\mathrm{Tr}[\exp(-H_0/k_BT)]}\ .$$

F_1 is an upper bound on the actual free energy F. The *stationary condition* for the free energy requires that

$$\frac{d}{d\phi}F_1=0\ .$$

This results in the following expression for ϕ:

$$\phi=\frac{\int_{\varepsilon-R_T}^{\infty}\exp(-u^2/2D)(d^2/du^2)V(R_T+u)du}{\int_{\varepsilon-R_T}^{\infty}\exp(-u^2/2D)du}\ . \tag{1}$$

Equation (1) shows that ϕ is a weighted *average of the force constant* over possible displacements from the position of equilibrium R_T, at temperature T. ε is the hard core of the potential. D is the mean-square displacement from equilibrium. By using $\partial F_0/\partial(\phi/2)=\langle u^2\rangle_0$, we obtain the following result:

$$D\equiv\langle u^2\rangle_0=\frac{\hbar}{2m\omega}\coth\left[\frac{\beta\omega}{2}\right]\ , \tag{2}$$

with $\beta=\hbar/k_BT$, m is the reduced mass of the two molecules, and ω is obtained from

$$m\omega^2=\phi\ . \tag{3}$$

At temperature T the position of equilibrium R_T is determined self-consistently [2,1]. In order to determine R_T we have chosen the following prescription: since in Eq. (1) $(R_T-\varepsilon)/\sqrt{D}\gg1$, we can neglect integrated terms due to the exponential factor and the equation is written as

$$\phi=-\frac{d}{dR_T}\times\frac{\int_{\varepsilon-R_T}^{\infty}\exp(-u^2/2D)[-(d/dR_T)V(R_T+u)]du}{\int_{\varepsilon-R_T}^{\infty}\exp(-u^2/2D)du}\ ,$$

i.e., ϕ is the negative derivative of the *average force;* the condition to determine R_T is that the average force vanishes,

$$-\frac{d}{dR_T}\left[\frac{\int_{\varepsilon-R_T}^{\infty}\exp(-u^2/2D)V(R_T+u)du}{\int_{\varepsilon-R_T}^{\infty}\exp(-u^2/2D)du}\right]=0\ . \tag{4}$$

The quantity in large parentheses is an average of the potential and the equilibrium R_T is the position where the averaged potential becomes minimum. For a given temperature T, Eqs. (1)–(4) are iterated until a self-consistent solution is reached.

III. POTENTIAL OF MEAN FORCE FOR IONS IN SOLUTION

Consider a solution of salt ions. The free energy of a fixed ion of type i at a distance r from another fixed ion of type j is the PMF. The degrees of freedom of the surrounding medium are statistically averaged giving the free energy of this pair as a function of temperature and concentration. This result can be derived starting from the general expression for the free energy [4]. The trace operation in the quantum-mechanical expression of the preceding section becomes an integral over phase space in the classical limit. Therefore the free energy F is obtained from

$$\int\exp\left[\frac{F-E(p,q)}{k_BT}\right]d\Gamma=1\ , \tag{5}$$

where $E(p,q)$, the energy of the system, is a function of the coordinates and momenta of all solvent molecules and ions that constitute the solution. The integral is over the phase space denoted by $d\Gamma=dpdq/(2\pi\hbar)^n$. By fixing the coordinates and momenta of the two ions a distance r apart and integrating over the rest of the phase space Γ', we get

$$\exp\left[\frac{-w(r)}{k_BT}\right]\equiv\int\exp\left[\frac{F-E(p',q';r)}{k_BT}\right]d\Gamma'\ , \tag{6}$$

which defines the PMF, $w(r)$. It is the free energy when the two ions are fixed. The quantity r acts as a parameter. Upon integration over $\mathbf{r}$ the free energy is obtained, i.e.,

$$F=-k_BT\ln\left[\int\exp\left[\frac{-w(r)}{k_BT}\right]\frac{d\mathbf{r}}{L^3}\right]\ ,$$

where L is a constant with units of length. Taking the derivative with respect to r in Eq. (6) and arranging terms, we get

$$\int[\delta(F+w(r))-\delta E(p',q';r)]\times\exp\left[\frac{F+w(r)-E(p',q';r)}{k_BT}\right]d\Gamma'=0\ .$$

It follows that

$$\delta w(r)=\left[\int\frac{\partial E}{\partial r}\exp\left[\frac{F'-E}{k_BT}\right]d\Gamma'\right]\delta r\equiv-f_r\delta r\ .$$

We omit the function arguments inside the integration to simplify the notation. For a system kept at constant temperature T the reversible work is given by the change in the free energy. Then f_r, the *average* force related to a change in the parameter r, is defined by the above expression. We then find that $w(r)$ is the PMF corresponding to r, $\partial w(r)/\partial r=-f_r$.

The ion solution can be thought of as a gas of charged hard spheres of radius $\sigma/2$ in a continuous medium, the solvent. At low concentrations, the PMF is a Debye-Hückel *screened Coulomb* interaction (DH). At high concentrations ($\approx 2M$), *hard-sphere correlations* (HS) become important. As an illustration, the following analytical expression of PMF suggested by Olivares and McQuarrie [5] and used by Soumpasis [6] shows these features:

$$w_{ij}(r)=w_{ij}^{\mathrm{HS}}(r)+z_i e \psi_j^{\mathrm{DH}}(r) \ . \qquad (7)$$

The second term in Eq. (7) is

$$\psi_j^{\mathrm{DH}}(r)=\frac{z_j e}{\epsilon(1+\kappa\sigma)} \frac{\exp[-\kappa(r-\sigma)]}{r} \ . \qquad (8)$$

The first term is

$$w_{ij}^{\mathrm{HS}}(r)=-k_B T \ln g_{ij}(r) \ , \qquad (9)$$

where $g_{ij}(r)$ is the pair-correlation function of a hard-core potential and to first order in $\rho\sigma^3$ it is given by

$$g_{ij}(r)=0, \quad r \le \sigma \ ,$$

$$g_{ij}(r)=1+\frac{4\pi}{3}\rho\sigma^3\left[1-\frac{3}{4}\frac{r}{\sigma}+\frac{1}{16}\frac{r^3}{\sigma^3}\right], \quad \sigma < r \le 2\sigma \ ,$$

$$g_{ij}(r)=1, \quad 2\sigma < r \ .$$

The definitions used above are the following. The proton charge, $|e|=4.8032\times 10^{-10}$ esu; z_i, a positive or negative number giving the charge of an ion of type i; ϵ, the dielectric constant of the solvent; ρ, the total number of ions per unit volume and $\rho=\sum_{i=1}^{2}\rho_i$, where ρ_i is the number density of ions of type i; $\sigma/2$, the hard-core radius of the ions; κ^{-1} is the Debye-Hückel screening length, given by

$$\kappa=\left[\frac{4\pi e^2}{k_B T\epsilon}\sum_{i=1}^{2}\rho_i z_i^2\right]^{1/2} \ .$$

The length κ^{-1} characterizes the range of the electrostatic interaction.

A discussion and the justification of Eq. (7) can be found in Ref. [5] on p. 151, where its use at relative high concentrations ($\approx 2M$) is supported by numerical calculations. Even a $2M$ solution is, however, still sufficiently dilute to use the low-density approximation for $g_{ij}(r)$ given under Eq. (9). For example, let us consider the simple case of a solution of a salt, lithium chloride, in water. The salt completely dissociates in $+|e|$ and $-|e|$ ions. The ionic radii of the elements that form the salt are approximately 1.8 Å for Cl and 0.6 Å for Li [7]. These radii are smaller than the radii of the hydrated ions. For a concentrated solution of lithium chloride the hydrated ion radii corresponding to a distance of coordinated water have been reported from neutron and x-ray studies [8]: 3.2±0.2 Å for Cl^- and 2.2±0.3 Å for Li^+. The sums of the hydrated radii are 4.4, 5.4, and 6.4 Å for the pairs Li^+-Li^+, Li^+-Cl^-, and Cl^--Cl^-, respectively. With a minimum separation σ of 5.4 Å for a Li^+-Cl^- pair and a salt concentration of $2M$, $\rho\sigma^3 \approx 0.38$ and this value will give us an estimate of the upper-limit densities required in this approximation. Throop and Bearman [9] have evaluated the solution to the Percus-Yevick equation numerically and tabulated the radial distribution function for the hard-sphere potential. The analytical expression for this function is given in Ref. [10,9]. Their calculation shows that for $\rho\sigma^3=0.3$ the expression for $g_{ij}(r)$ given under Eq. (9) is a plausible one. A computer program that evaluates the Percus-Yevick correlation function with a modification [11] which is in good agreement with Monte Carlo data for hard spheres is provided in Appendix D of Ref. [12]. The PMF obtained when using in Eq. (9), the Percus-Yevick correlation function is displayed in Fig. 1 where the interaction of two *negative* charges, $-|e|$, is plotted as a function of the separation r. The two anions are immersed in a salt solution of concentration c and a solvent dielectric constant ϵ. The salt dissociates to yield free $+|e|$ and $-|e|$ charges. For high enough concentration of the salt, the potential is attractive in the range $\sigma < r \le 2\sigma$ because the Coulomb repulsion is screened and the term $w_{ij}^{\mathrm{HS}}(r)$ becomes important. The attraction in this range increases with increasing temperature. This feature can be examined more closely by writing the PMF [Eq. (7)] with substitution of the expression under Eq. (9) into $w_{ij}^{\mathrm{HS}}(r)$. For the two anions in the range $\sigma < r \le 2\sigma$, it is found

$$w(r)=-k_B T\left\{\ln\left[1+\bar{\rho}\frac{4\pi}{3}\left[1-\frac{3}{4}\bar{r}+\frac{1}{16}\bar{r}^3\right]\right] - \frac{\Delta\bar{\rho}^{-1/3}}{1+\bar{\kappa}}\frac{\exp[-\bar{\kappa}(\bar{r}-1)]}{\bar{r}}\right\} ,$$

where $\Delta=e^2\rho^{1/3}/\epsilon k_B T$, $\bar{\kappa}=\kappa\sigma$, $\bar{\rho}=\rho\sigma^3$, and $\bar{r}=r/\sigma$. With $\bar{\kappa}^2=4\pi\Delta\bar{\rho}^{2/3}$, there are two independent parameters in this expression, i.e., Δ and $\bar{\rho}$. ρ is the number concentration of the ions which is $\rho_+ + \rho_-$. Since $\rho^{-1/3}$ is the average separation between two nearest ions, Δ is the ra-

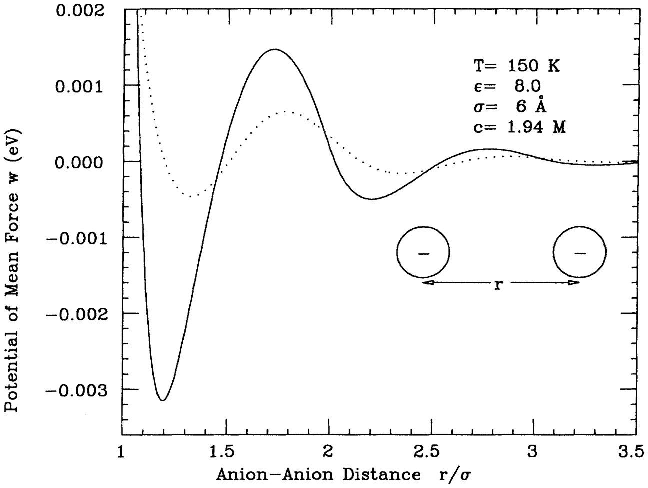

FIG. 1. The PMF of two anions near the dissociation temperature is plotted as a function of the separation. Solid lines (——) represent the PMF [from Eq. (7)] using the Percus-Yevick pair-correlation function (Refs. [10–12]) in Eq. (9). The corresponding average potential from the self-consistent equations which was defined at the end of Sec. II is shown in dotted lines. At high temperatures the average potential is shallower than the PMF due to the large fluctuations centered at R_T. The charge of each anion is $-|e|$. ϵ is the dielectric constant of the solvent, c is the molar salt concentration, σ is the hard core of the potential, and ρ the number concentration of the ions, $\rho\sigma^3 \approx 0.50$ (compared to the maximum of 1.41).

tio of the Coulomb interaction to the mean thermal energy $k_B T$. A bar on the variables denotes that length has been normalized by the hard-core distance σ.

Using the self-consistent-field equations we have calculated the thermal equilibrium separation between the anion centers R_T as a function of temperature using the PMF resulting from the first order in $\rho\sigma^3$ and from the Percus-Yevick pair-correlation functions. [In these calculations we used the Percus-Yevick approximation rather than the expression under Eq. (9) because $\rho\sigma^3$ was larger than 0.3, the value for which the expression under Eq. (9) is valid.] These calculations are shown in Fig. 2. The insets show the rms displacement and the force-constant parameter. The integration in Eq. (1) required an analytic expression for the potential at $r<\sigma$; in this region the potential is repulsive. We added a repulsive exponential that does not change significantly the minimum of the PMF and provides a strong hard core at $r<\sigma$; its form is the following: $A\exp(-\lambda r)$, where $A=1000$ eV and $\lambda=18$ Å^{-1}. In the temperature interval displayed in Fig. 2, R_T is within the attractive part of the potential. The anion-anion separation increases with temperature and gets out of the range $\sigma<r\leq 2\sigma$; this happens at 86 and 155 K in each of the calculations. Beyond these temperatures a self-consistent solution no longer exists and this point is used as a criterion for the dissociation temperature. The example displayed has a value of $\rho\sigma^3\approx 0.50$ (compared to the maximum of 1.41, the value for close-packed spheres [13]). This value of $\rho\sigma^3$ is beyond the estimated limits for an approximation that uses $g_{ij}(r)$ up to first order in $\rho\sigma^3$. At high temperatures, the difference between the two curves increases with temperature as expected. The averaged potential as it was defined at the end of Sec. II is shown in Fig. 1. At finite temperatures the fluctuations centered at R_T make the average of the potential shallower than the PMF.

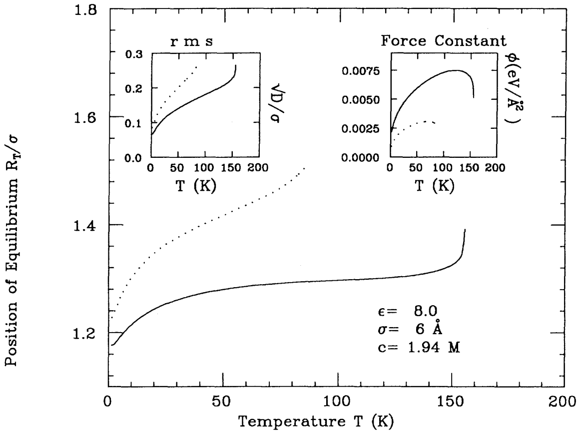

FIG. 2. The results of the self-consistent equations with a potential for two anions. The thermal separation R_T is plotted as a function of the temperature. The insets show the rms displacement $\sqrt{D}$ and the force constant ϕ as functions of temperature. Dissociation occurs when a self-consistent-field-equation solution no longer exists; this fact corresponds to the vanishing of the force constant and a sharp increase of R_T and $\sqrt{D}$. The dotted lines show the results using the PMF calculated from the pair-correlation function $g_{ij}(r)$ up to first order in $\rho\sigma^3$. Solid lines correspond to a calculation where the pair-correlation function in the Percus-Yevick approximation was used (Refs. [10–12]). In this example $\rho\sigma^3\approx 0.50$.

The attractive term discussed in this section is due to an entropy effect that turns out to be important when electrostatic repulsion is screened. This feature can be qualitatively explained by a geometrical consideration of the *excluded volume* of the fixed ions. This is shown in Fig. 3 and discussed in the next section. The PMF given in Eq. (7) will be used to treat the systems that we consider in an ionic environment.

IV. ATTRACTIVE INTERACTION DUE TO HARD-CORE EXCLUSION

In the following discussion we examine the implications of picturing the solution as charged hard spheres in a continuous medium. Because of the high degree of screening at the densities we have considered the charge does not take part in the argument, and what is important is the finite size of the ions. Consider a gas consisting of $N+2$ hard-sphere ions of radius $\sigma/2$. In this system the centers of two ions cannot get closer than a distance σ, the hard core of the potential. To get the free energy of the gas when two arbitrary ions are kept fixed a distance r apart, we have to integrate over the phase space due to the other ions in Eq. (6). The integration over the momenta can be performed; it gives a term independent of r. The potential energy is zero until the distance of approach of two ions is less than σ when it becomes infinite. Therefore the exponential inside the integral is 1 whenever two ions are at a distance larger than σ, otherwise it vanishes. Omitting r-independent terms due to the momenta integration and to the indistinguishability of the particles we have the following expression for the free energy:

$$W=-k_B T\ln\left[\int{}'\frac{d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_N}{V^N}\right],$$

where the integration is restricted in the sense that no two ions can get closer than a distance σ. Consider a sphere of radius σ centered at every ion, the *excluded sphere* of the ion [14]. This idea was used by Boltzmann in calculating corrections to a van der Waals equation of state. The volume of an excluded sphere is eight times the volume of an ion and it defines the space where the center of a second ion cannot penetrate, as illustrated in Fig. 3. It is possible to get an approximate value of this integral at low concentrations, when the excluded spheres are not touching. In this regime the mean ion separation $\rho^{-1/3}$ is large compared to σ and the total volume V is much larger than the volume occupied by the spheres. The integral is approximately equal to $[(V-Nv_0)/V]^N$, where $v_0=(4\pi/3)\sigma^3$ is the volume excluded by a sphere. Expanding the logarithm and keeping first-order terms in the density $\rho=N/V$, the free energy per particle is

$$w\approx k_B T\rho v_0\ . \tag{10}$$

This expression is independent of *r*. If the two fixed ions are closer than 2σ, *r*-dependent corrections become important, due to the *overlap* of the excluded spheres, as shown in Fig. 3. These corrections are given in Eq. (9) by $w^{\mathrm{HS}}(r)=-k_BT\ln g_{ij}(r)$, where $g_{ij}(r)$ is the pair-correlation function of a hard-core potential to first order in the density [15]. It can be shown that when *r* is in the range $\sigma<r\le 2\sigma$, Eq. (9) can be written

$$w^{\mathrm{HS}}(r)=-k_BT\ln[1+\rho v_1(r)]\ ,$$

where v_1 is the space where the two excluded spheres of the fixed ions overlap. In the limit when this space of overlap v_1 is small with respect to the average volume occupied by an ion, $v_1(r)\rho\ll 1$, the expression for the free energy becomes approximately

$$w^{\mathrm{HC}}(r)\approx -k_BT\rho v_1(r)\ . \tag{11}$$

This is a function of *r* and it *decreases* when the overlap $v_1(r)$ increases, that is, when the two ions get closer together. When the two ions are close the excluded volume of the pair is *less* than when the are far apart, by an amount that corresponds to the overlap of the spheres, which is the space that is excluded to the other ions.

For a separation *r* between two spheres, the volume of overlap can be calculated [14,15] from

$$v_1(r)=2\pi\int_{r/2}^{\sigma}[\sigma^2-x^2]dx$$
$$=\frac{4\pi}{3}\sigma^3\left[1-\frac{3}{4}\frac{r}{\sigma}+\frac{1}{16}\left[\frac{r}{\sigma}\right]^3\right]\ ,$$

where $\sigma<r\le 2\sigma$. The range of concentrations for which one expects this approximation to hold is when the gas is dilute enough to assure that multiple close encounters do not occur in more than pairs.

The excluded volume for *n* spheres that overlap would be $nv_0-\sum v_1+\sum v_2-\cdots-\sum v_{n-1}$, where v_{n-1} is the common space to *n* spheres. For a hard-sphere gas there is a maximum of 12 spheres that can have a mutual overlap and that occurs at the maximum concentration of $\sqrt{2}/\sigma^3$. The hard-sphere pair-correlation function has also been calculated in the so-called mean spherical approximation for the case when the radii of the two fixed ions differ. See Ref. [16] on bottom of p. 6282. The excluded volume when the spheres overlap is obtained if we replace σ by $(\sigma_1+\sigma_2)/2$ in the expressions, where σ_1 and σ_2 are the diameters of the two ions. Assuming $\sigma_1>\sigma_2$ and keeping σ_1 fixed, the effect would decrease if the diameter of the second ion σ_2 decreases.

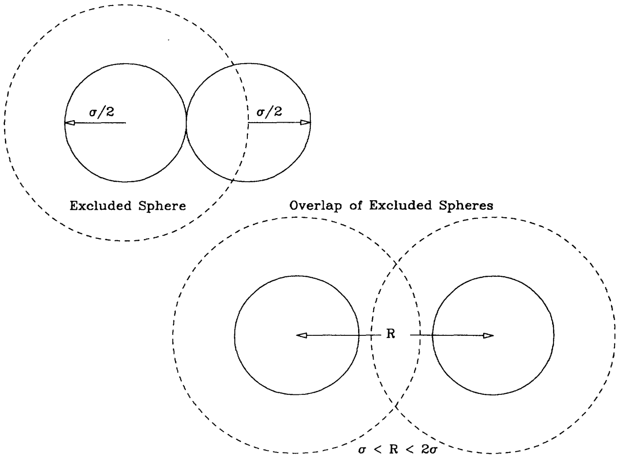

FIG. 3. Excluded volume to other ions in solution. When the two fixed ions are far away ($\ge 2\sigma$) the total excluded volume is larger than when they are at close distances because there is an overlap of the spheres. The minimum separation is σ.

V. HYDROGEN-BONDING DISSOCIATION IN IONIC SOLUTION

The general considerations given at the beginning of Sec. III for the two ions can be made for the case of a pair of molecules. Therefore, besides the two-anion case already discussed, we have chosen three hydrogen-bonded systems: two negative charges, two ammonia molecules, and two water molecules. The four geometric arrangements are shown in Fig. 4. The hydrogen bond is formed by a hydrogen atom in between the centers of negative charge that are at a distance *r*. In the original treatment by Gao and Prohofsky [17] the hydrogen bond of the two ammonia molecules was given by a Morse potential. In that calculation the molecules were taken as two point masses. The Morse potential fit the results of a quantum-mechanical calculation for this particular geometric arrangement of the molecules [18]. In the case of water we use a Morse potential that fits published energy values [19]. The Morse potential is given by $V(r)=V_0(\{1-\exp[-\alpha(r-R_0)]\}^2-1)$. The Morse parameters for the two-anion case were $V_0=3.48$ kcal/mol, $\alpha=1.22$ Å^{-1}, $R_0=3.37$ Å; for ammonia $V_0=3.48$ kcal/mol, $\alpha=1.22$ Å^{-1}, $R_0=3.37$ Å; and for water

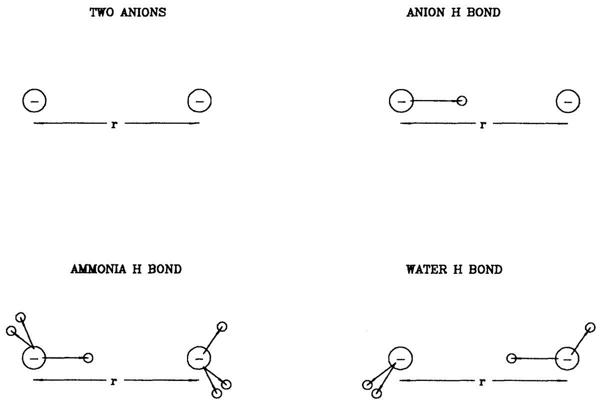

FIG. 4. The geometry for each system is sketched, two anions and three hydrogen-bonded pairs. The two tetragonal ammonia molecules are arranged in a symmetrical staggered conformation. In the water case the axis of the H bond is in the plane of one molecule, the plane of the second molecule makes a 30° angle with a plane perpendicular to this axis. The small circles represent positive-charge sites.

$V_0=5.2$ kcal/mol, $\alpha=1.43\ \text{Å}^{-1}$, $R_0=3.07$ Å. In the figures we have used eV as a unit of energy, 1.0 eV $=23.06$ kcal/mol, 1 eV/Å$^2=16.02$ kdyn/cm. We obtained the electrostatic contribution of the bonding and estimated the effects of the medium by including the PMF. It is assumed that the Morse potential consists of two *effective* contributions, a hard core and a long-range electrostatic interaction

$$V_{\text{Mor}}=V_{\text{HC}}+V_{\text{Coul}}\ , \tag{12}$$

where V_{Coul} represents a sum of the pair Coulomb interaction between the charges of the bonded pair. The effects of interaction with the solution are introduced by replacing the electrostatic interaction V_{Coul} by the PMF. In solution, the hydrogen-bond potential is

$$V=V_{\text{HC}}+V_{\text{PMF}}\ , \tag{13}$$

where V_{PMF} represents the sum of the charge interactions using the PMF [Eq. (7)]. Subtraction of Eq. (12) from Eq. (13) yields the potential to be used in the self-consistent mean-field theory, Eqs. (1)–(4),

$$V=V_{\text{Mor}}+[V_{\text{PMF}}-V_{\text{Coul}}]\ . \tag{14}$$

This last expression depends upon the distance r between the negative charge centers of the bonded pair. In Fig. 5, two examples of this expression at finite salt concentration and temperature are displayed by dot-dashed lines. The corresponding thermal average potentials defined at the end of Sec. II are shown by dotted lines. At zero concentration, Eq. (14) reduces to a Morse potential which is shown by a solid line.

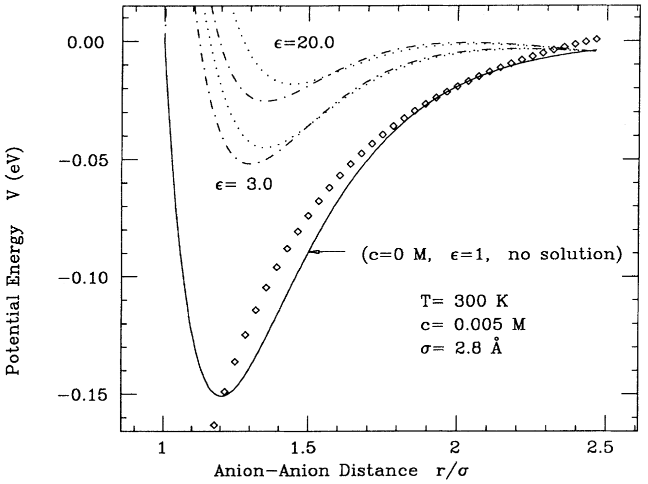

FIG. 5. Energy of interaction of two anions with a H bond. Dot-dashed lines (—·—·—·) represent the potential obtained from Eq. (14), the salt concentration is 0.005M, and temperature $T=300$ K. Two values of the dielectric constant are displayed, $\epsilon=20.0$, $\epsilon=3.0$, and $\sigma=2.8$ Å. The dotted lines display the thermal average potential that corresponds to Eq. (14). They were obtained from the expression given at the end of Sec. II. At zero salt concentration the energy is a Morse potential. Increasing the concentration, the position of the minimum increases and the potential gets shallower. The ◇ depicts the electrostatic energy V_{Coul}, calculated from charge pair interactions.

Following the arguments given at the beginning of Sec. III, Eq. (14) is the free energy for a given separation r. The Morse potential used in the calculations is written as $V_{\text{Mor}}=4V_0(\{1-\exp[-\bar{\alpha}(\bar{r}-1)]\}^2-1)$, where $\bar{\alpha}=\alpha\sigma$, $\bar{r}=r/\sigma$, $\sigma=R_0-(1/\alpha)\ln 2$. Here, σ represents the distance where the Morse potential vanishes and it corresponds to the minimum separation where the electrostatic interactions are considered in these calculations. At smaller distances only the repulsive part of the Morse potential operates. σ is approximately 2.8 Å in the ammonia and the hydrogen-bonded anion cases; and 2.6 Å in the water case. A bar in the formulas means that length is scaled by σ. We have assumed a radius of $\sigma/2$ for each molecule in the bonded pair. In the range $\sigma<r\leq 2\sigma$ the PMF for the two-anion system is

$$V_{\text{PMF}}=-k_BT\left\{\ln\left[1+\bar{\rho}\frac{4\pi}{3}\left[1-\frac{3}{4}\bar{r}+\frac{1}{16}\bar{r}^3\right]\right]\right.$$
$$-\frac{\Delta\bar{\rho}^{-1/3}}{1+\bar{\kappa}}\exp[-\bar{\kappa}(\bar{r}-1)]$$
$$\left.\times\left[\frac{1}{\bar{r}}-\frac{\delta}{\bar{r}-\bar{h}}\right]\right\},$$

where we follow definitions similar to those used in the two-anion case of Sec. III. The additional symbols are $\delta=|q_H/e|$, q_H is the effective positive charge that stabilizes the bonding and $\bar{h}=h/\sigma$ is the separation from this positive point charge to the closest anion which remains fixed. Charges are $-|e|$ for each anion and $q_H=0.98|e|$, $|e|$ is the proton charge. The fixed separation from the negative ion to the positive center was set to $h=0.15$ Å. For the water and ammonia systems we have used the conformations and parameters given in the references [18,19] as it is shown in Fig. 4. The ammonia molecules were placed in a staggered geometry [18]. For water, the oxygen atoms are in the plane of one molecule and the plane of the second one makes a 30° angle with a plane perpendicular to the bond axis [19]. For water, $h=0.956$ Å and the O–H–O angle is 105.2°. For ammonia, $h=0.991$ Å and the N–O–N angle is 115.9°. The partial charges for the ammonia molecule are $0.32|e|$ for hydrogen and $-0.96|e|$ for nitrogen. For water, they are $0.33|e|$ for hydrogen and $-0.66|e|$ for oxygen. The results of the self-consistent set of equations for the two hydrogen-bonded anions are shown in Figs. 6 and 7. For all hydrogen-bonded systems, the thermal averaged separation of the negative centers R_T represents the *H-bond length* at equilibrium, $\sqrt{D}$ is the root-mean-squared displacement (rms) and ϕ the force constant from Eqs. (1)–(4). These quantities are functions of temperature and salt concentration. In these calculations the systems were considered dissociated at the temperature where a self-consistent solution no longer exists which coincides with the vanishing of the force constant ϕ and with a sharp increase in the equilibrium separation and the rms deviation $\sqrt{D}$. In the examples the maximum value of the density parameter was $\rho\sigma^3=0.13$ which makes the PMF calculated from the expression for $g(r)_{ij}$ under Eq.

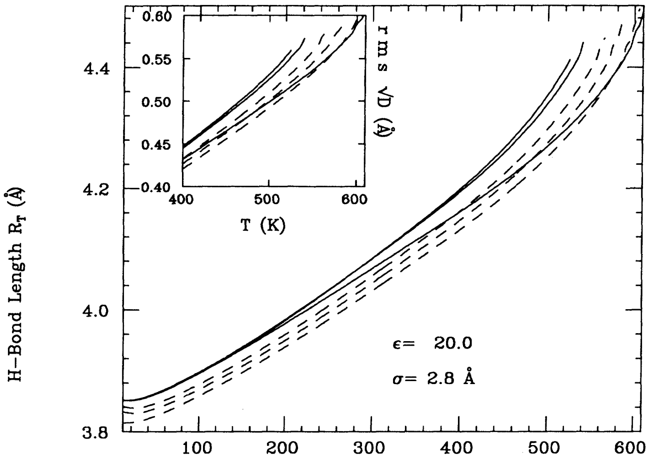

FIG. 6. H-bond dissociation transition as a function of temperature and salt concentration (c). The thermal separation R_T between the two anions with a H bond and the corresponding rms displacement $\sqrt{D}$ (in the inset) are displayed. For low concentration, the dashed lines (— — —) represent the following concentrations and temperatures associated with a rms displacement of 10% of R_T (in parentheses): 0M (390 K), 0.001M (385 K), 0.005M (375 K); the dissociation temperature *decreases* with increasing concentrations. In high concentration, the solid lines (——) represent 1M (360 K), 2M (360 K), 5M (375 K); the dissociation temperature *increases* with increasing concentration. The hard core σ is ≈ 2.8 Å and $\epsilon = 20.0$ in these calculations. For a molar concentration of the salt of 5M, $\rho\sigma^3 \approx 0.13$ (compared to the maximum of 1.41).

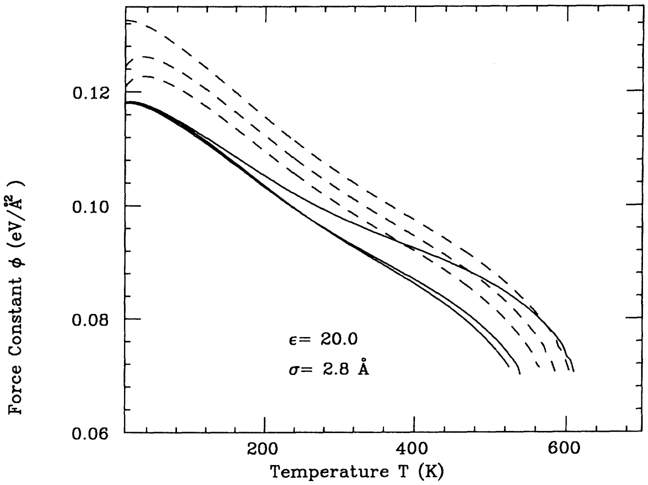

FIG. 7. H-bond force constant as a function of temperature and salt concentration is shown. The corresponding force constants of Fig. 6 are displayed. For low concentration, the dashed lines (— — —) represent the following concentrations and temperatures associated with a rms displacement of 10% of R_T (in parentheses): 0M (390 K), 0.001M (385 K), 0.005M (375 K); the dissociation temperature *decreases* with increasing concentration. In high concentration, the solid lines (——) represent 1M (360 K), 2M (360 K), 5M (375 K); the dissociation temperature *increases* with increasing concentration. The hard core σ is ≈ 2.8 Å and $\epsilon = 20.0$ in these calculations. For a concentration of the salt of 5M, $\rho\sigma^3 \approx 0.13$ (compared to the maximum of 1.41 of close-packed spherical ions).

(9) a suitable approximation. A calculation using an analytical expression for $g(r)_{ij}$ up to second order in the density [20] showed no essential changes. In the figure captions, the temperature where the rms displacement reaches 10% of R_T is noted to nearly coincide with the beginning of the transition. The reduced mass parameter used for the two-anion case corresponds to a hydrogen-bonded pair of Cl^- (≈ 18 amu). The calculations are almost insensitive to a mass change. For example, if in the calculations shown we use the mass parameter corresponding to a pair of F^- the transition temperature would be lower by 1 or 2 K.

VI. DISCUSSION OF RESULTS

The present self-consistent-field approximation is able to describe a dissociation transition in the systems that we treated. We have shown that the temperature of dissociation can be defined as the temperature where the self-consistent equations no longer have a solution; this corresponds to the vanishing of the force-constant parameter and a sharp increase in the equilibrium separation and the fluctuations. The way of introducing the PMF in Eq. (14) is consistent with the mean-field nature of the approximation. We have stressed the importance of introducing non-Coulomb contributions to the free energy due essentially to the finite size of the ions or molecules. The competition between intermolecular forces other than van der Waals have been pointed out in the literature [6,16,21,22]. Attractive terms that are dependent on the counterion concentration have been found. This attractive interaction is an entropy effect. For two equally charged planar electrical double layers [21,22] there is evidence of structure in the effective interaction that shows attractive contributions. Whether or not this mechanism is similar to the one found for the two-anion case requires further investigation. The example of two anions shows a regime where the non-Coulomb contributions are important. See Fig. 1. In this case, the hard core of the potential is given by the parameter $\sigma = 6$ Å. This value is close to twice the hydrated radius of Cl^-, corresponding to a distance of coordinated water, reported from x-ray and neutron studies in concentrated LiCl solutions, $r_{Clh} \approx 3.2$ Å [8]. In a concentrated solution and within separations of a few angstroms, we expect the value of the dielectric-constant parameter determined by the molecular polarizability of bound water molecules of the hydration shells. The dielectric-constant parameter used in this example was set to $\epsilon = 8.0$. This value is of the order of the dielectric constant attributed to water of hydration, as it is suggested in the literature [23]. The results obtained for the three hydrogen-bonded systems are qualitatively similar. The ammonia system is somewhat unrealistic in the sense that when immersed in a polar medium such as water the ammonia molecule becomes ammonium (NH_4^+). The ammonia system was chosen in order to make comparisons with the initial calculation of Gao and Prohofsky [17]. A typical calculation with the anion H-bond system is shown in Figs. 5–7. The energy of the H bond that corresponds to Eq. (14) is shown for different concentrations in Fig. 5. The Morse parameters for the H bond of the example displayed in Figs. 5–7 give an attractive energy that is weak compared to the H bond of water. We have considered this example since there is experimental evidence that weak H-bond energies are commonly found in biological systems [18,24]. These curves show correctly the limiting form of the Morse potential, when no medium is considered. As it is seen in Fig. 5, the form of the potential is strongly dependent on the dielectric-constant parameter ϵ. We have chosen a lower value for ϵ than the bulk dielectric constant of water and close its saturation arising from molecular polarizability that displays a reasonable temperature of melting. On increasing the concentration the well gets shallower and the position of the minimum is increased. This effect is due to the ion screening of Coulomb interaction of the H bond. The dissociation of the hydrogen-bonded anions is displayed in Figs. 6 and 7 as a function of temperature for various concentrations and $\epsilon=20.0$. In the range of *low salt concentrations,* an increase of the concentration produces a decrease in the temperature of the transition, a result to be expected because of Debye-Hückel screening. This fact is seen by the trend of the dashed lines in Figs. 6 and 7. In the hydrogen-bonded water molecules the dissociation-temperature shift is consistent with the trend in the melting-point depression of water which is expected when salt is dissolved [25]. This behavior of charge shielding might be responsible for the fact that DNA is dissociated in water at room temperature in the absence of excess salt. In this low-concentration regime the excluded-volume effects are not important. In the regime of *high salt concentration* the shift is reversed; on increasing the concentration the dissociation transition temperature increases. This fact is shown by solid lines in the figures. In this high-concentration limit the Coulomb interaction is screened out and it is the attractive term due to the hard-core exclusion that tends to stabilize the bond. The use of Eq. (9) with the hard-core correlation to first order in $\rho\sigma^3$ is justified since the maximum value of this parameter is 0.13 as it is noted in the figure captions.

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