McMillan–Mayer theory for solvent effects in inhomogeneous systems: Calculation of interaction pressure in aqueous electrical double layers

Roland Kjellander, Alexander P. Lyubartsev, and Stjepan Marčelja

Citation: *The Journal of Chemical Physics* **114**, 9565 (2001); doi: 10.1063/1.1366639

View online: <http://dx.doi.org/10.1063/1.1366639>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/114/21?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Ionic asymmetry and solvent excluded volume effects on spherical electric double layers: A density functional approach](#)

J. Chem. Phys. **140**, 204510 (2014); 10.1063/1.4876002

[The tail effect on the shape of an electrical double layer differential capacitance curve](#)

J. Chem. Phys. **138**, 144704 (2013); 10.1063/1.4799886

[Molecular solvent model of cylindrical electric double layers: A systematic study by Monte Carlo simulations and density functional theory](#)

J. Chem. Phys. **129**, 154707 (2008); 10.1063/1.2981057

[Density-functional theory of spherical electric double layers and \$\zeta\$ potentials of colloidal particles in restricted-primitive-model electrolyte solutions](#)

J. Chem. Phys. **120**, 7223 (2004); 10.1063/1.1676121

[Forces between like-charged walls in electrolyte solution: Molecular solvent effects at the McMillan–Mayer level](#)

J. Chem. Phys. **112**, 8939 (2000); 10.1063/1.481535

The logo for AIP APL Photonics. It features the letters 'AIP' in a large, white, sans-serif font, followed by a vertical orange bar and the words 'APL Photonics' in a smaller, white, sans-serif font. The background is a red gradient with a bright yellow sunburst effect in the upper right corner.

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief

McMillan–Mayer theory for solvent effects in inhomogeneous systems: Calculation of interaction pressure in aqueous electrical double layers

Roland Kjellander

Department of Chemistry, Physical Chemistry, Göteborg University, S-412 96 Göteborg, Sweden

Alexander P. Lyubartsev

Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

Stjepan Marčelja

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

(Received 6 July 2000; accepted 27 February 2001)

We demonstrate how to use the McMillan–Mayer theory to include solvent effects in effective solute–solute interactions for inhomogeneous systems, extending a recent derivation [S. Marčelja, *Langmuir* **16**, 6081 (2000)] for symmetric planar double layers to the general case. In the exact treatment, the many-body potential of mean force between the solute molecules can be evaluated for an inhomogeneous reference system in equilibrium with pure bulk solvent. The reference system contains only solvent and a finite number, n , of fixed solute molecules and it has an external potential that in some cases is different from that of the original system. It is discussed how the n -body potential of mean force between the ions for the relevant cases of large n values can be approximated by a sum of effective singlet and pair interactions evaluated in the presence of, on average, all n ions, i.e., at finite concentration. In examples considered in this work we use effective interionic pair potentials evaluated from bulk electrolyte calculations at finite electrolyte concentrations. We calculate the contribution to the double layer interaction pressure arising from the interaction between ions dissolved in aqueous electrolyte. In cases of moderate or high surface charge, calculations show several new effects. At small surface separations one finds attractive and then strongly repulsive contributions. For surface charge density around one negative charge per 70 Å² the full results for pressures resemble “secondary hydration force” measured in classical experiments in 1980s. When there is a tendency for ions to adsorb at the surfaces there is a marked change in behavior. The force is then oscillatory, reminiscent of results obtained with the surface force apparatus at low electrolyte concentration. © 2001 American Institute of Physics. [DOI: 10.1063/1.1366639]

INTRODUCTION

Extensive experimental evidence supports the importance of the structure of discrete aqueous solvent in double layer interaction.¹ Perhaps the most dramatic example is the oscillatory force profile between charged mica surfaces in KCl solution measured by Pashley and Israelachvili² in 1983. Most solvent effects remain, however, poorly understood, in the sense that there is no quantitative theory capable of reproducing the data.

Over the last decade, simulations of aqueous solutions of ions were gradually improved, resulting in realistic potentials of mean force between ion pairs.³ In an important conceptual step, Adelman^{4,5} in the 1970s and later Lyubartsev and Laaksonen⁶ introduced effective potentials between ions in molecular solvent, which improve on the potentials of mean force and accurately reproduce thermodynamic properties of aqueous solutions.⁶ Friedman⁷ and Høje and Stell⁸ have explored some properties of this effective potential. These advances promised development of sufficiently simple and accurate methods to treat the problem of aqueous double layers. Marčelja⁹ used potentials of mean force between ions in aqueous solvent obtained in molecular dynamics simula-

tions to show that the short-range part of the potential between ions in solution is a plausible source of the experimentally observed “secondary hydration force.”

Double layer models including ion–ion potentials of mean force can also be constructed using density functional methods.¹⁰ This approach can obtain many results from a procedure that is easier to apply than the anisotropic hypernetted chain (aHNC) approximation¹¹ used in Ref. 9 and in the present work. The approximation quite accurately evaluates average effects of the short-range potential between ions. In its present form it is particularly suitable for applications involving monovalent electrolytes where ion–ion correlations are relatively weak. In the cases where such correlations are important more accurate methods like the aHNC approximation are needed.

In the current work the solvent is treated on the McMillan–Mayer level, i.e., the solvent degrees of freedom are not treated explicitly, but enter implicitly in an effective potential between the ions. Provided many-body potential of mean force is used for the effective ionic interactions, this is a formally exact way of including molecular solvent for bulk systems.^{12,13} However, in practical applications one normally

does not use many-body potentials but approximates them with a sum of pair potentials, which at infinite dilution corresponds to the superposition approximation. The customary approximation is to use the potential of mean force between two ions in bulk solvent, i.e., at infinite dilution, as the pair potential. An even simpler approximation is the primitive model, where the long-range asymptotic form of interaction potential between two ions in bulk solvent is used for all distances outside hard core contact (i.e., the Coulomb potential in a dielectric medium).

An improvement over the primitive model can be achieved by using for all distances the potential of mean force for two ions in bulk solvent at infinite dilution. This improves the accuracy of the model at short separations. In earlier similar work by Marčelja⁹ the required potential was taken from simulations of two ions in molecular solvent. Very recently, Otto and Patey¹⁴ treated double layer problems using the potential obtained from a model of molecular solvent. Both studies subsequently used the aHNC approximation for evaluation of the pressure.

The McMillan–Mayer theory has recently been formally adapted for treatments of two equal, interacting double layers in planar geometry by one of us.¹⁵ Thereby the validity of this approach for this kind of inhomogeneous systems has been demonstrated. It was also shown that the interaction pressure between equal planar surfaces can be written as a sum of two terms: one arising from water between uncharged surfaces and the other from hydrated ions between charged surfaces. This exact treatment indicates possible approximations that are better than the simple superposition mentioned above. In the current paper we shall generalize the approach and elaborate on the approximate potentials.

Furthermore, for some typical examples we shall calculate the major contribution to the pressure between interacting charged surfaces in aqueous electrolyte solutions: the term contributed by ions interacting with each other via the potentials of mean force. While the current work is similar in intent to that of Refs. 9 and 14, we provide formal justification for the method, use more accurate potentials and explore the sensitivity of the potentials to coion concentration and the presence of counterions. We also present first qualitative results of the effects of specific counterion adsorption on the double layer pressure.

MCMILLAN–MAYER THEORY FOR INHOMOGENEOUS SYSTEMS

Let us consider an inhomogeneous solution (not necessarily an electrolyte) enclosed in a volume V and in equilibrium with a bulk solution of known composition, i.e., a reservoir with a given chemical potential for each species. The inhomogeneity may, for example, be caused by an external potential (like a particle-wall potential) $V_s(\mathbf{x}, \mathbf{\Omega})$ where s is the species index, $\mathbf{x}$ is the three-dimensional position coordinate, and $\mathbf{\Omega}$ is the set of molecular orientation angles for a molecule. The species index takes the value 0 for the solvent and 1,..., M for the M solute species. For simplicity in notation we shall limit ourselves to two solute species ($M=2$); the results below can be easily extended to the general case of M species. We shall denote the coordinates for molecule i

of species j as $\mathbf{R}_{i,j} \equiv (\mathbf{x}_{i,j}, \mathbf{\Omega}_{i,j})$. The total interaction energy when the system contains $(m_0, m_1, m_2) \equiv \mathbf{m}$ molecules of the various species with coordinates $(\{\mathbf{R}_{i,0}\}_{i=1}^{m_0}, \{\mathbf{R}_{i,1}\}_{i=1}^{m_1}, \{\mathbf{R}_{i,2}\}_{i=1}^{m_2}) \equiv \{\mathbf{R}\}$ is denoted $U_{\mathbf{m}}(\{\mathbf{R}\})$. When the external potential for species s is $V_s(\mathbf{R}) \equiv V_s(\mathbf{x}, \mathbf{\Omega})$ this energy can be written

$$U_{\mathbf{m}}(\{\mathbf{R}\}) = U_{\mathbf{m}}^{\text{int}}(\{\mathbf{R}\}) + \sum_{s=0}^M \sum_{i=1}^{m_s} V_s(\mathbf{R}_{i,s}), \quad (1)$$

where $U_{\mathbf{m}}^{\text{int}}(\{\mathbf{R}\})$ is the total internal (intramolecular and intermolecular) energy of interaction of the system. The arguments below are, however, not dependent on that $U_{\mathbf{m}}(\{\mathbf{R}\})$ can be written in this form, but are valid for more general forms of the external potential that may include many-body effects and thereby depends on the coordinate of all particles in a more complicated manner (e.g., like when the particles polarize the wall). Furthermore, the molecules do not need to be rigid as implicitly assumed here.

The grand partition function of the system is given by

$$\Xi(\mathbf{z}) = \Xi(z_0, z_1, z_2) = \sum_{m_0, m_1, m_2 \geq 0} \frac{(z_0)^{m_0} (z_1)^{m_1} (z_2)^{m_2}}{m_0! m_1! m_2!} \times \int \exp[-\beta U_{\mathbf{m}}(\{\mathbf{R}\})] d\{\mathbf{R}\}, \quad (2)$$

where z_s is the activity of species s , $\mathbf{z} = (z_0, z_1, z_2)$, $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, and T is the absolute temperature. The integral is over the volume V and the entire orientational space for each particle and $d\{\mathbf{R}\}$ denotes the volume and normalized orientation differentials. The activity is $z_s = \rho^0 \exp[\beta(\mu_s - \mu_s^0)]$, where μ_s is the chemical potential of species s , μ_s^0 is the standard chemical potential, and ρ^0 is the standard density (e.g., the unit density). As the standard state we select the ideal bulk gas mixture with density ρ^0 for all components, i.e., $\exp(\beta \mu_s^0) = \Lambda_s^3 \Gamma_s \rho^0 / q_s$, where Λ_s is de Broglie thermal wavelength, Γ_s is the contribution from the thermal orientational motion if any, and q_s is the intramolecular partition function.

For a bulk solution (i.e., when $V_s \equiv 0$ for all s) the standard McMillan–Mayer argument^{12,13} gives the following relationship between $\Xi(\mathbf{z})$ and the grand partition function $\Xi(\mathbf{z}^*)$ at a different set of activities $\mathbf{z}^* = (z_0^*, z_1^*, z_2^*)$

$$\frac{\Xi(\mathbf{z})}{\Xi(\mathbf{z}^*)} = \sum_{m_0, m_1, m_2 \geq 0} \frac{1}{m_0! m_1! m_2!} \left(\frac{z_0 - z_0^*}{\gamma_0^*} \right)^{m_0} \times \left(\frac{z_1 - z_1^*}{\gamma_1^*} \right)^{m_1} \left(\frac{z_2 - z_2^*}{\gamma_2^*} \right)^{m_2} \times \int \exp[-\beta w^{(\mathbf{m})}(\{\mathbf{R}\}, \mathbf{z}^*)] d\{\mathbf{R}\}, \quad (3)$$

where $\gamma_s^* = z_s^* / \rho_s^*$ is the activity coefficient and ρ_s^* is the bulk density of species s [i.e., belonging to the set of densities $(\rho_0^*, \rho_1^*, \rho_2^*)$ that gives the activities (z_0^*, z_1^*, z_2^*)] and where the potential of mean force $w^{(\mathbf{m})}$ is defined from

$$w^{(m)}(\{\mathbf{R}\}, \mathbf{z}^*) = -k_B T \ln \left[\frac{\rho^{(m)}(\{\mathbf{R}\}, \mathbf{z}^*)}{(\rho_0^*)^{m_0} (\rho_1^*)^{m_1} (\rho_2^*)^{m_2}} \right] \quad (4)$$

and $\rho^{(m)}(\{\mathbf{R}\}, \mathbf{z}^*)$ is the grand canonical m -particle distribution function for the system at activities $\mathbf{z}^*$. Since this argument¹³ relies only on a Taylor expansion in $\mathbf{z}$, it can be carried through unchanged for an inhomogeneous system ($\nu_s \neq 0$) provided the functional form of the interaction $U_m(\{\mathbf{R}\})$ is the same for both sets of activities $\mathbf{z}$ and $\mathbf{z}^*$, i.e., the internal and the external potentials are the same. In this case one can select ρ_s^* as the bulk density in the reservoir (then the zero of the potential of mean force corresponds to infinite separations in bulk reservoir solution). Thus Eq. (3) is valid also for an inhomogeneous solution.

We now select $z_0^* = z_0$, $z_1^* = 0$ and $z_2^* = 0$, i.e., $\Xi(\mathbf{z}^*) = \Xi(z_0, 0, 0)$ refers to the inhomogeneous system in equilibrium with pure bulk solvent, the density of which is adjusted to make $z_0^* = z_0$. Now all terms on the right-hand side (rhs) of Eq. (3) that contain index 0 are identically zero and the remaining terms contain only potentials of mean force between solute molecules placed in an inhomogeneous solvent in presence of the external potential. We have

$$\frac{\Xi(\mathbf{z})}{\Xi(z_0, 0, 0)} = \sum_{\substack{m_1, m_2 \geq 0 \\ m_0 = 0}} \frac{1}{m_1! m_2!} \left(\frac{z_1}{\gamma_1^0} \right)^{m_1} \left(\frac{z_2}{\gamma_2^0} \right)^{m_2} \times \int \exp[-\beta w^{(m)}(\{\mathbf{R}\}, z_0, 0, 0)] d\{\mathbf{R}\}, \quad (5)$$

where the activity coefficient γ_s^0 is that of an infinitely dilute bulk solution, i.e., $(\gamma_s^0)^{-1}$ is the single ion partition function for interactions with the solvent. Thus $\Xi(\mathbf{z})$ and thereby the properties of the inhomogeneous solution at activities (z_0, z_1, z_2) can be calculated from $\Xi(z_0, 0, 0)$ and the potentials of mean force between the solute molecules as obtained at the activities $(z_0, 0, 0)$. The solvent degrees of freedom are not explicitly included on the rhs of Eq. (5) but are implicit in $w^{(m)}$.

For electrolyte systems in some geometries, like planar double layers near infinitely large charged walls, zero ionic activities do not imply zero ionic concentrations and one has to proceed somewhat differently from the derivation above. The counterion concentration remains nonzero in the vicinity of the wall surface even at equilibrium with pure solvent; i.e., the counterions cannot be removed by dilution in these cases. Even at finite bulk concentrations one has to modify the analysis above. Let us as an example consider an inhomogeneous electrolyte in a slit between two infinitely large planar walls (i.e., in the limit of infinite volume V of the slit which, however, has a finite width equal to the surface separation).

The equilibrium condition is that each ionic species has equal chemical potential in the bulk and in the slit and, at the same time, that the inhomogeneous system is electroneutral (including the surface charges). Even a minuscule charge imbalance would imply an enormous electrostatic potential difference between the slit and the bulk when they are far apart (for instance separated by a thick wall). A nonelectro-neutral system between the walls would, in fact, have an

infinite energy since the Coulomb interaction between a finite charge and an infinitely large planar surface with non-zero surface charge is infinitely large (the integral of $1/r$ diverges). The existence of a neutralizing charge in the bulk far away would make the total electrostatic energy finite, but huge. If the ionic single species chemical potentials in the bulk and in the slit would be different so that, for example, counterions leave the electroneutral slit, a potential difference $\Delta\psi$ would be immediately setup that prevents this from happening and electroneutrality would be maintained. As a result, the chemical potential of species s in the slit would gain an extra contribution $q_s \Delta\psi$, where q_s is the ionic charge, making the total chemical potential of species s equal to that in bulk. Note that such a potential difference would not affect the value of the mean chemical potential $\mu_{\pm}$, so electroneutral combinations of anions and cations can freely equilibrate between the bulk and the slit without being affected by $\Delta\psi$. Furthermore, the value of $\Delta\psi$ is determined by the equilibrium density distribution and corresponds to configurations with the most probable number of particles per unit area in the slit. Thus $\Delta\psi$ is a state dependent quantity; it depends, for example, on the bulk composition and therefore on the activities there.

The contribution $q_s \Delta\psi$ to the chemical potential gives rise to a factor $\exp(\beta q_s \Delta\psi)$ in the activity, $z_s = \rho^0 \exp[\beta(\mu_s - \mu_s^0)]$. By defining ‘‘intrinsic activity’’ of the inhomogeneous system as $\zeta_s \equiv z_s \exp(-\beta q_s \Delta\psi) = \rho^0 \exp[\beta(\mu_s - \mu_s^0 - q_s \Delta\psi)]$ the contribution from the potential difference $\Delta\psi$ is removed. Let us apply this to the limit $z_s^* \rightarrow 0$ for $s = 1, 2$ discussed above, i.e., equilibrium with pure solvent in the bulk. The potential difference is $\Delta\psi^*$ when the bulk activities are (z_0^*, z_1^*, z_2^*) . When z_1^* and $z_2^* \rightarrow 0$ the magnitude of the potential difference $\Delta\psi^*$ grows without bounds (it has sign opposite to that of the counterion charge), which forces counterions to remain in the slit to ensure electroneutrality even when $z_s = 0$. Thereby $\Delta\psi^*$ makes $z_s^* \exp(-\beta q_s \Delta\psi^*) \neq 0$ for $s =$ counterions in the limit $z_s^* \rightarrow 0$, i.e., the intrinsic counterion activity ζ_s^* in the slit remains nonzero and electroneutrality is maintained.

The potential differences $\Delta\psi$ at activities $\mathbf{z}$ and $\Delta\psi^*$ at activities $\mathbf{z}^*$ can be alternatively be regarded as being contained in the external potential. The McMillan–Mayer argument that leads from Eq. (2) to Eq. (3) for an inhomogeneous system, requires that the external potential does not depend on $\mathbf{z}$. Since $\Delta\psi$ is nonzero and state dependent in the geometries in question, this argument is not generally valid as presented above. Furthermore, the derivation of Eq. (5) requires that no infinities arise for the potentials when z_1^* and $z_2^* \rightarrow 0$, so this equation cannot be used as it stands. By making a Taylor expansion in the intrinsic activities instead, one can, however, prove a similar result (see Appendix)

$$\frac{\Xi(\mathbf{z})}{\Xi^\dagger(z_0, 0, 0)} = \sum_{\substack{m_1, m_2 \geq 0 \\ m_0 = 0}} \frac{1}{m_1! m_2!} \left(\frac{z_1}{\gamma_1^0} \right)^{m_1} \left(\frac{z_2}{\gamma_2^0} \right)^{m_2} \times \int \exp(-\beta [w^{(m)}(\{\mathbf{R}\}, z_0, 0, 0) + (m_1 q_1 + m_2 q_2) \Delta\psi]) d\{\mathbf{R}\}, \quad (6)$$

where $\Xi^\dagger$ is the partition function and $w^{\dagger(\mathbf{m})}$ is the potential of mean force of an inhomogeneous reference system with a different external potential than the original system (it differs by a constant contribution χ being added to the external potential, see below). The potential difference $\Delta\Psi$ in Eq. (6) is defined by [cf. Eq. (A3)]

$$\Delta\Psi = \Delta\psi - \chi - \Delta\psi^\dagger.$$

where $\Delta\psi^\dagger$ is the potential difference between the bulk and the reference system at activities $(z_0, 0, 0)$.

The reference system is selected such that the electrostatic part of the external potential originates from an external charge distribution with zero net charge. In such a system there are no counterions that have to remain to ensure electroneutrality when the bulk electrolyte concentration goes to zero. Therefore no complication with the potentials occurs in the limit of zero bulk electrolyte concentration. Furthermore, the external potential should differ only by a constant χ from the original one.

In planar geometry we can obtain such a reference system from our original system by adding two equal, planar and uniform surface charge distributions, each with a surface charge density $\sigma^\dagger$. These two sheets of surface charges—additional to those already present—should be placed such that our inhomogeneous system with volume V is located entirely between them, i.e., in the region where the electrostatic potential from the $\sigma^\dagger$ sheets is constant. The additional constant potential χ originates from these added external surface charge densities. (The separation between the $\sigma^\dagger$ sheets can otherwise be arbitrarily large since χ is independent of this separation.) Note that χ does not cause any forces on the particles in the inhomogeneous system; it only affects the equilibrium condition with the bulk solution. To make the net external charge of the reference system equal to zero, $-2\sigma^\dagger$ must be equal to the total external charge per unit area of our original system.

As an example, consider the case of an electrolyte solution between two planar, infinitely large walls with equal uniform surface charges σ . Then the reference system has two walls with zero surface charge (we put the additional surface charge densities $\sigma^\dagger$ at each plane of surface charge σ and we have $\sigma^\dagger = -\sigma$). This is the case considered in Ref. 15, where the constant potentials were implicitly included in the activities. In Eq. (6) we see explicitly that the electrostatic potential from the surface charges of the original system has to be added to $w^{\dagger(\mathbf{m})}$, which describes the ion interactions for a system with uncharged walls (this point was not made clear in Ref. 15). Since χ is constant, the external forces on all molecules in the reference system are identical to those in the original system.

As a second example, consider two planar walls that have different uniform surface charge densities. In this case the reference system has walls with nonzero surface charge densities, but the walls have equal but opposite charge densities making the sum of charges of the two walls equal to zero. The electroneutral solvent molecules will not feel any net force from the wall charges, but in general they will feel a torque if, for example, they have a dipolar charge distribu-

tion. This external torque is, of course, the same as in the original two-wall system.

Third, we take a system with two equal planar walls with discrete surface charges. Then the reference system in Eq. (6) has two walls, each of which has a charge distribution that is the sum of the discrete charge distribution and the uniform surface charge density $\sigma^\dagger$. The average net charge density of each surface is, however, zero. The potential of mean force $w^{\dagger(\mathbf{m})}$ is then evaluated for fixed ions in pure solvent between such walls. Again, the external forces are the same as in the original two-wall system—it is only the equilibrium condition with the bulk reservoir that is different and thereby the composition between the walls. Finally, we consider a system with, for instance, spherical geometry like a charged sphere in contact with an electrolyte solution. Then Eq. (5) applies (since the counterions are removed from the system at infinite dilution) and the “reference system” has exactly the same external potential as the original system, i.e., the external electrostatic potential of the reference system is that of the charged sphere.

Equations (5) and (6) imply that the free energy (grand potential) of our original system is the sum of the free energy of the reference system and a part that is evaluated by using the potential of mean force between the solvated ions instead of the original (bare) ion–ion interaction potential. Thus other thermodynamic quantities like the pressure will also be the sum of two such parts. For example, the net interaction pressure between two charged walls separated by distance d in an electrolyte with activities $\mathbf{z}$ is given by

$$P(d; \mathbf{z}) = [P^\dagger(d; z_0, 0, 0) - P_{\text{bulk}}(z_0, 0, 0)] + [P^{w^\dagger}(d; \mathbf{z}) - P_{\text{bulk}}^w(\mathbf{z})], \quad (7)$$

where $P^\dagger(d; z_0, 0, 0)$ is the interaction pressure between the two walls in the reference system (with only solvent present), $P_{\text{bulk}}(z_0, 0, 0)$ is the bulk pressure of pure solvent, $P^{w^\dagger}(d; \mathbf{z})$ is the interaction pressure between the walls calculated with potential of mean force $w^\dagger$ for solvated ions and $P_{\text{bulk}}^w(\mathbf{z})$ is the corresponding pressure for bulk. For double layers with only counterions present $P_{\text{bulk}}^w(\mathbf{z})$ is zero, but in presence of salt it is nonzero.

THE MANY-BODY POTENTIAL OF MEAN FORCE

Let us now consider the implications of the findings above for the potential of mean force in the reference system, which is to be used to evaluate $\Xi(\mathbf{z})$ of the original system via Eq. (6) [the same arguments apply to Eq. (5) and $w^{(\mathbf{m})}(\{\mathbf{R}\}, z_0, 0, 0)$]. We shall assume that species 1 and 2 are ionic (but this is not essential for the conclusions). Let us consider the potential of mean force between the ions $w^{\dagger(\mathbf{m})}(\{\mathbf{R}\}, z_0, 0, 0)$ with $m_0 = 0$ (no solvent molecules are held fixed), i.e., $\mathbf{m} = (0, m_1, m_2)$. To evaluate this function we should have (m_1, m_2) ions of the two species fixed at coordinates $\{\mathbf{R}\}$ in the reference system. All solvent molecules are free to move around and to leave or enter the system, which is in equilibrium with pure bulk solvent at activity z_0 . No ions except the fixed ones are present, which means that there are no mobile ions that cause screening of the electrostatic field. We have only dielectric screening

caused by the mobile solvent molecules. The electrostatic field from all charged particles (including the external charges) is a superposition of the fields from fixed charges and it is modified due to the polarization response of the solvent. This response is to be evaluated when the solvent molecules feel the interactions with each other and with the (m_1, m_2) fixed ions and the external potential of the reference system. In addition to the electrostatic forces, the mean force on each ion has contributions from the nonelectrostatic interactions including momentum transfer from solvent molecules that collide with the ion. This is again to be evaluated in the presence of the interactions between the solvent and the fixed ions as well as the external potential.

The dominant contribution to the sum in Eq. (5) or (6) comes from the terms where $\mathbf{m}$ has values that are at or very close to the average $\langle \mathbf{m} \rangle \equiv (\langle m_0 \rangle, \langle m_1 \rangle, \langle m_2 \rangle)$ of the original system at activities $\mathbf{z}$. Furthermore, the integral in each of these terms is by and large dominated by contributions where the coordinates $\{\mathbf{R}\}$ are distributed in agreement with the most probable distribution. Thus, the most important many-body potentials of mean force are those that describe interactions between ions distributed like they are on average in the original system.

In practice one cannot accurately evaluate the many-body potentials of mean force for the reference system and then use them for the evaluation of the properties of the original system. One has to resort to approximations and a simple one is to approximate each many-body potential as a sum of effective singlet (ion-wall) and pair (ion-ion) potentials. To obtain a reasonably fair representation of the many-body potential, one should consider the fact that the effective interaction between an ion and the wall and between two ions should be evaluated when there is a huge number of other ions present, as we saw above. These ions are fixed and do not cause any screening in the reference system (the "bare" electrostatic interactions between these ions are indeed pairwise additive according to Coulomb's law), but the dielectric screening due to the polarization response of the solvent is affected by the presence of these ions. Thus the dielectric screening is not well approximated by that at infinite dilution (as done in, e.g., the primitive model), but is better represented by that of an electrolyte solution at finite concentration where the solvent molecules are partially immobilized by (or at least have preferential orientations and locations due to) the interactions with the large number of ions present. As we shall see, the long range part of effective pair interactions between the ions in bulk is given by a Coulomb potential with a dielectric constant ϵ_r that changes with increasing concentration roughly like the experimentally determined decrease of ϵ_r for bulk electrolytes.

For inhomogeneous systems one should consider that the immobilization should be larger where the ion concentration is high and that it is dependent on which ion species are present. Therefore, one should in some way consider the local concentration of ions in the double layer when approximating, for example, the electrostatic interactions between pairs of ions there. A similar argument applies for the mean forces due to nonelectrostatic interactions. The external potential also affects the polarization response of the solvent

and the mean force contributions from the nonelectrostatic forces between the particles. Furthermore, the presence of a wall, beyond which no solvent molecules can pass in the reference system, implies that so-called image charge effects have to be included explicitly when the many-body potentials are approximated as sums of effective pair and singlet potentials (the latter includes the self-interaction between each ion and its image). In this paper we shall, however, as a first step neglect all these influences of the external potentials and use effective pair interactions evaluated in bulk electrolytes. The motivation for this neglect is that we are primarily interested in trends and qualitative features of the solvent effects on the ion-ion interactions in double layers.

PAIRWISE POTENTIALS OF MEAN FORCE BETWEEN IONS

The question is now what effective pair interaction between ions should be used to approximate the many-body potential of mean force between them. Different approximations could provide fair or good predictions for different equilibrium properties; no such approximation can be successful for *all* properties. Most detailed available information about a bulk electrolyte is normally that contained in the ionic pair distribution functions. To use this information one selects an effective ion-ion potential $u_{ij}^{\text{eff}}(r)$ that gives the same pair distributions as the full many-body potential of mean force. Since there is a one-to-one relationship between pair potentials and the resulting pair distributions (assuming pairwise additivity of the former), there is a unique solution to this inversion problem.

This gives a rationale for the effective pair potential evaluated from the accurate ionic pair distributions in aqueous solution by means of reverse Monte Carlo techniques developed by Lyubartsev and Laaksonen.⁶ The statistical mechanical basis for this kind of effective pair potential was first demonstrated by Adelman.^{4,5} In the approach of Lyubartsev and Laaksonen the ionic pair distributions are first obtained from simulations of an electrolyte solution with molecular water. Then the effective interionic pair potential is obtained with an iterative MC technique where a trial pair potential is varied until the resulting ion-ion pair distribution agrees with the one previously obtained. The idea is then to use this potential for calculations in other systems.

The resulting effective potential $u_{ij}^{\text{eff}}(r)$ between a pair of ions fulfils some basic requirements discussed above (see also Refs. 4, 5, 7, and 8): (i) for large ion-ion separations the molecular structure of the solvent is unimportant and the potential must approach the macroscopic Coulomb law, reduced in magnitude by the intervening dielectric. There is no exponential screening arising from the presence of other ions; (ii) the strength of the macroscopic dielectric constant is influenced by the composition of the solution, i.e., the presence of other ions.

Let us now investigate such effective potentials obtained for bulk solutions, which we will use for calculations of double layer systems. Effective potentials were obtained from simulations with SPC model of water using molecular dynamics method as described earlier.¹⁶ As the calculated

double layer pressure depends quite sensitively on the details of ion-ion potentials we have carefully considered the accuracy of these potentials.

It is convenient to consider the effective ion-ion potential in an electrolyte as consisting of two additive terms. The first term is the classical Coulomb force in a dielectric, which is of course the correct asymptotic form. The remainder is a short-range contribution due to the presence of solvent and the dispersion interaction between the ions. It also contains some short-ranged effects of ion-ion correlations, which arise because the many-body potential of mean force between the ions is not pairwise additive.⁸

The accuracy of simulated potentials is limited by the finite size of the simulated system. As expected, it is very difficult to evaluate correctly the weak but still important contributions to the potential at ion-ion separations of about 10 Å and larger. But even at smaller separations, finding the short-range part of the potential is not straightforward. To determine the short-range correction we need to know the dielectric constant ϵ_r that governs the strength of the Coulomb term. The dielectric screening depends on salt concentration and ϵ_r is not separately available. In simulation the system size limits the accuracy of assessing the asymptotic strength of the Coulomb interaction and thus ϵ_r .

In double layer problems, the short-range part of ion-ion potential will be most significant near highly charged surfaces where counterions are close to each other and very few coions are present. We have therefore tested the influence of anions and of the electrolyte concentration in a bulk system where the only species were Na^+ ions and water. Molecular dynamics simulation as described in Ref. 16 was adjusted to accommodate a uniform background of opposite charge that balances the system.

The results for the effective potential are presented in Fig. 1. This figure should be compared to the effective potential for Na^+-Na^+ pair obtained in 0.5 M solution of NaCl (Fig. 2 and Ref. 16). The results for Na^+-Na^+ pair in Na^+ only system and in NaCl are almost the same except perhaps at highest concentrations. We conclude that in determining Na^+-Na^+ effective potential Cl^- ion is only of secondary importance. We can also conclude that the short-range part of the effective Na^+-Na^+ potential is relatively insensitive to the electrolyte concentration.

The values of ϵ_r used to draw Fig. 1 were selected in order to give symmetrical oscillatory short-range part of the potential. They are decreased compared to the value for pure water, corresponding approximately to the experimental decrease of ϵ_r in concentrated NaCl solutions.¹⁷ As simulation data do not extend to large separations, other similar values for ϵ_r could have been chosen to fit a Coulomb tail to each curve. If in reality the Na^+-Na^+ pair potential is slightly attractive, due to favorable arrangement of water dipoles between the ions, the curves are correspondingly shifted. The purpose of Fig. 1 is to demonstrate the fairly weak dependence of the short-range part of the potential on electrolyte concentration. As we shall see, it is also only weakly dependent on the presence or absence of coions. On the other hand, the long-range Coulomb part of the potential increases with

FIG. 1. Upper four curves (symbols), from top down: Effective potential between two Na^+ ions in 8 M, 4 M, 1 M, and 0.5 M solution of one-component aqueous electrolyte vs center-to-center separation r . Coulomb part of the interaction is shown for 0.5 and 8 M cases (dashed lines). Dielectric screening is stronger in dilute solutions. The dielectric constants assumed for the simulation system were 39.0, 51.5, 66.7, and 78.0, respectively. Lower curves: Short-range interaction obtained after subtracting Coulomb potential from the full effective potential. Oscillatory short-range potential is more strongly damped at higher concentrations.

concentration as indicated in both experimental¹⁷ and simulation values of the dielectric constant.

The effective potentials for the three kinds of ion pairs in 0.5 M NaCl solution are shown in Figs. 2–4. The short range potential for these pairs can be more accurately determined because all three pairs must have a common ϵ_r and show a reasonable behavior at short separations. Using $\epsilon_r = 78$ leads to results where short-range interaction for the Na^+-Na^+ pair is slightly attractive and for Na^+-Cl^- pair slightly re-

FIG. 2. Effective potential for the Na^+-Na^+ pair in 0.5 M NaCl electrolyte. The full potential (open symbols), Coulomb part (dashed line), and short-range part (full symbols) are shown separately. The first minimum corresponds to contact between ions, second to solvent-separated pair and so on. Data from Ref. 16.

FIG. 3. Same as Fig. 2 but for the $\text{Na}^+ - \text{Cl}^-$ pair.

pulsive. Other values of ϵ_r lead to less plausible results. Note that the short-range part of the potentials for 0.5 M in Figs. 1 and 2 are quite similar. The presence of Cl^- in the latter case has not affected it much.

Can we justify this choice? Independent simulations¹⁸ for pure water using the same flexible SPC water model gave the value $\epsilon_r = 82.5$. Experiments indicate that in 0.5 M NaCl solutions the dielectric constant is lowered from 78 in pure water to about 72 in the electrolyte solution.¹⁷ Lowering the simulation value by about the same amount leads to $\epsilon_r \approx 76.5$ in reasonable agreement with the value obtained above.

PRESSURE BETWEEN CHARGED SURFACES

The double layer pressure between surfaces is a very sensitive quantity that depends on the choice of the model, the level of approximation used in solving the model and the

accuracy of the calculation. In order to explore the commonly neglected effect of the aqueous solvent on the double layer interaction it is therefore best to calculate the pressure under a variety of conditions.

From Eq. (7) follows (see also Ref. 15) that the exact net pressure in aqueous double layers is the sum of the solvent and ionic contributions. Each contribution can be calculated as the difference in the pressure between surfaces and the pressure in bulk (the latter corresponds to the pressure at infinite separation between the surfaces).

While the approximate procedure to calculate pressure as outlined above is very straightforward, at present we do not have all required input quantities to make a quantitative comparison with experiments. The first contribution in Eq. (7), i.e., the difference in pressure between the bulk water and water between surfaces, is not known with sufficient precision and will not be considered in this paper.

The second term, which corresponds to the difference in pressure between the reference bulk ionic system and the ionic system between the surfaces, depends on ion-ion and ion-surface potentials in the presence of the solvent. The former potentials have been estimated from simulations in bulk conditions. Although the effect of surfaces on the pair potential has not been studied in detail, existing simulation of ion-ion potentials in presence of DNA¹⁹ suggest that the effect is not large.

The ion-surface potentials of mean force are presently not available. These potentials depend very much on the species of the ion and the nature of the surface, and currently we have insufficient reliable data to attempt to include it in the calculation. Insight into the likely behavior can be obtained from the studies involving montmorillonite or vermiculite clay surfaces²⁰ which have chemical composition similar to mica. In simulations of Na^+ or Ca^{2+} approach to a clay surface, both “inner sphere” and “outer sphere” adsorption complexes have been observed.

In order to obtain some qualitative information about the effect of specific counterion adsorption on the double layer interaction, a simple square well adsorption potential was included in some of the calculations. This adsorption potential mimics specific counterion-surface interactions that, of course, are not included in the ion-uniform surface charge interaction. The adsorbed ions were allowed to interact with each other and with free ions via the same ion-ion potential of mean force evaluated in bulk solvent. The corresponding results have to be considered as only an indication of the possible wealth of behavior.

The calculations for double layers were performed with the effective potentials shown in Figs. 2–4, which are those of the smaller simulation run for NaCl at 0.5 M electrolyte concentration in Ref. 16. The short-range part of the potential was approximated by analytical functions and used in all subsequent double layer calculations. Dielectric constant for the Coulomb part of the potential was $\epsilon_r = 78.36$ and temperature was 298.15 K. For simplicity, these potentials were used also for double layer calculations at other electrolyte concentrations. Simulations have shown that within the available accuracy, the short-range parts of the potentials at 0.5 M and 1.0 M are the same. Assuming the same at lower

FIG. 4. Same as Fig. 2 but for the $\text{Cl}^- - \text{Cl}^-$ pair.

concentration therefore incurs only a minor error. However, the Coulombic part of the potential is, as we have seen, affected by a change in the dielectric constant with concentration. For example, in NaCl solutions, dielectric constant decreases to¹⁷ 66.7 at 1M. This decrease of bulk dielectric constant is not significant for the presented examples except for the last case of 1M solution shown in Fig. 13. Since in the present calculations we are mainly interested in qualitative trends, we have neglected this.

In order to calculate the pressure we used aHNC theory of electrical double layers developed earlier by two of us to study effects of ion correlations.¹¹ The short-range potential between the ions is included into the calculation in the HNC approximation

$$g_{ij} = \exp[h_{ij} - c_{ij} - u_{ij}^{\text{eff}}/k_B T], \quad (8)$$

where g_{ij} is the anisotropic pair distribution of the inhomogeneous electrolyte, $h_{ij} = g_{ij} - 1$, c_{ij} is the anisotropic direct correlation function and u_{ij}^{eff} is the effective ionic pair potential, in this work obtained from bulk. The latter is split in three parts

$$u_{ij}^{\text{eff}} = u_{ij}^{\text{Coul}} + u_{ij}^{\text{Hyd}} + u_{ij}^{\text{Core}},$$

where u_{ij}^{Coul} is the dielectrically screened Coulomb force (with the ϵ_r value obtained above) and the last two terms constitute the short-range part of the effective potential, which is split into two terms for computational convenience. They correspond, respectively, to the hydration shell contributions, u_{ij}^{Hyd} , and the hard core potential of ions, u_{ij}^{Core} . In the numerical work, hard-core contact values were selected as 3 Å, 2.6 Å, and 4.4 Å for $\text{Na}^+ - \text{Na}^+$, $\text{Na}^+ - \text{Cl}^-$, and $\text{Cl}^- - \text{Cl}^-$ ion pairs, respectively.

The ionic contribution to pressure between the surfaces is given as

$$P_{\text{tot}} = P_{\text{kin}} + P_{\text{el}} + P_{\text{core}} + P_{\text{hyd}} - P_{\text{bulk}}. \quad (9)$$

The kinetic, electrostatic (Coulomb), core and bulk terms have been described earlier.²¹ The contribution of the hydration potential to the pressure is calculated from the correlation functions

$$P_{\text{hyd}} = - \sum_{i,j} \int_0^\delta dx \rho_i(x) \int_{-\delta}^0 dx' \rho_j(x') \times \int d\mathbf{r} \frac{\partial u_{ij}^{\text{hyd}}([r^2 + (x-x')^2]^{1/2})}{\partial x} g_{ij}(r, x, x'), \quad (10)$$

where ρ_i, ρ_j are the densities of ionic species, x is the direction normal to the surfaces which are located at $x = \pm \delta$ and r is the radial coordinate parallel to the surface.

Normally one should expect that short-range effects in ion-ion interaction would only be important for high surface charge density. To estimate in what range of surface charge densities they contribute the following simple argument can be used. The short-range part of the potential is significant for ion separations less than about 10 Å. If we would assume that all counterions that neutralize the surface charge are located in one single layer, the effect of short-range forces should first appear when average lateral separation between

FIG. 5. Ionic pressure in aqueous solvent between surfaces with a charge density of one negative charge per $135 \text{ \AA}^2$ in 0.1 M NaCl electrolyte. From top to bottom: PB result, aHNC result without short-range interaction between counterions, aHNC with the full interaction shown in Figs. 2–4. In this and all subsequent figures, zero separation is defined as a hard-core contact with one layer of counterions between the surfaces (i.e., a distance of 3 Å between hard surfaces).

counterions is around 9 or 10 Å. This corresponds to a surface charge density of $135 \text{ \AA}^2$ per unit charge (which is representative of the surface charge of montmorillonite clays). The effect becomes stronger with increasing surface charge density.

A calculation of the double layer pressure for surface charge density of $135 \text{ \AA}^2$ per unit charge and 0.1 M NaCl electrolyte concentration is shown in Fig. 5. The effect of hydration is indeed weak. The short-range part of the potential is just beginning to have an effect on the interaction of surfaces. In this and all subsequent figures, zero in the separation scale corresponds to the closest approach of the two surfaces to each other when a layer of counterions is located between them (they must remain there for reasons of electroneutrality). The closest approach is here taken as the hard-core diameter of the counterions (3 Å in this work). In a more general view where ions interact with surfaces, zero on the separation scale corresponds to twice the minimal counterion-surface separation.

However, a very different result is obtained if counterions tend to adsorb to the surfaces due to a specific adsorption potential in addition to the electrostatic interaction (Fig. 6). We modelled this counterion-wall potential as a square well, but other localized adsorption potentials lead to the same result. The width of the well was 0.16 Å (the thermal wavelength of the ion) and the depth was a free parameter. The specifically adsorbed counterions are mobile in the potential well and correlate fully with each other and with other ions. The number of adsorbed ions is determined from the condition of equal chemical potential for all counterions everywhere, which is intrinsic in the aHNC method. In Fig. 6 we chose the depth of the adsorption potential well for both ion species as $3 k_B T$. As can be seen, adsorbed ionic layers on interacting surfaces lead to oscillatory double layer interaction. With about half of the surface charge compensated by

FIG. 6. Ionic pressure between surfaces with a charge density of one negative charge per $135 \text{ \AA}^2$ and ion adsorption at the surfaces in 0.1 M NaCl electrolyte. Top curve: aHNC result without short-range interaction (the primitive model). Oscillatory curve: aHNC with full interaction. At the selected adsorption strength, 47% of the surface charge is compensated by adsorbed counterions (well depth $3k_B T$). Coion adsorption is negligible.

the specifically adsorbed counterion layer, one finds strongly oscillatory pressure with four minima clearly discernible. The oscillations stem from the oscillatory short-range interaction between ions in the solvent. They are not caused by surface-solvent-surface layering, which is a separate additive contribution [the first term of Eq. (7)] and not included in the calculation. When the counterions are not adsorbed specifically and a high counterion concentration therefore occurs in a wider region close to each wall, the oscillations are smeared out. As apparent in Fig. 6 they become very visible if they originate from ion-ion interactions in a well-defined narrow adsorption layer. In this example, the attraction at small separations is a well-known effect of correlations between ions in discrete layers adsorbed at the surfaces. The attraction is also present in models where solvent is described as a dielectric continuum, but the magnitude is modified by the molecular solvent.

What happens when electrolyte concentration is varied? We consider this question together with a change to higher surface charge in Fig. 7. With the exception of very high electrolyte concentrations, the behavior of double layer repulsion at short separations is only weakly dependent on concentration. In such cases it is sufficient to study the pressure as a function of surface charge and the affinity of counterions for adsorption at the surfaces. The example of 1 M electrolyte will be considered separately further down.

At $75 \text{ \AA}^2$ per unit charge the behavior of double layer interaction is already significantly affected by the short-range part of ion-ion interaction. Comparison with the PB theory and the primitive model is given in Fig. 8. Typical features include a decrease in repulsion in the separation range 6–12 $\text{\AA}$ and a change to very strong repulsion at shorter separations. The behavior of force is again strongly dependent on the adsorption strength of the counterion (Fig. 9), where stronger adsorption leads to more oscillatory pressure.

At this time it is convenient to consider separate contri-

FIG. 7. aHNC ionic pressure between negatively charged surfaces with charge density of one unit charge per $75 \text{ \AA}^2$ and different background electrolyte concentrations. Short-range ion-ion potential is included in the calculation but no specific ion adsorption. From top to bottom: aqueous NaCl electrolyte concentrations of 1 mM, 25 mM, 0.1 M, and 1 M. Notice the change to the log scale in this and the next figure.

butions in Eq. (9) to the overall pressure shown in earlier figures. Figure 10 shows separate terms for the typical case of $75 \text{ \AA}^2$ per unit charge and 0.1 M NaCl aqueous electrolyte. It can be seen that the hydration shell contribution P_{hyd} is mostly attractive, hard core is unimportant, and the return to strong repulsion is due to the kinetic term $P_{\text{kin}} = \rho_{\text{mid}} k_B T$, where ρ_{mid} is the total ion concentration at the midplane between the surfaces.

The oscillatory pressure between the surfaces calculated in cases with surface adsorption (Fig. 11) originates from the short-range part of the ion-ion potential between ions near one surface and those near the other surface [Eq. (10)]. In the presence of adsorption overall repulsion is much weaker, as

FIG. 8. Comparison between double layer pressure in different models. The surfaces are negatively charged with the charge density of one unit charge per $75 \text{ \AA}^2$ and the background aqueous electrolyte concentration is 0.1 M NaCl. From top to bottom: PB theory, aHNC without short-range interaction, aHNC with the full potential, aHNC with the full potential and adsorption. In this last case adsorption layer compensates 50% of the surface charge (well depth $2k_B T$).

FIG. 9. Effect of adsorption at surface charge density of one charge per $75 \text{ \AA}^2$ and the background aqueous electrolyte concentration is 0.1 M NaCl . From top to bottom: adsorption layers of 0, 50%, and 84%, respectively, of the surface charge (well depths $0.2k_B T, 4k_B T$).

attractive contributions to the pressure of comparable size arise from both the short-range potential and from electrostatic correlations.

The highest surface charge studied in these examples is $48 \text{ \AA}^2$ per unit charge, corresponding to the crystallographic charge of muscovite mica. At such high charge we find a region of surface separations where the interaction is attractive²² extending between about 4 and $10 \text{ \AA}$ (Fig. 12). Again, when the specific adsorption potential for counterions is turned on the pressure becomes oscillatory.

Finally, one should consider high electrolyte concentrations. The behavior of the pressure between surfaces with one unit charge per $75 \text{ \AA}^2$ in 1 M NaCl is shown in Fig. 13. Overall, the force is much weaker. It is attractive until very

FIG. 10. Different contributions to double layer pressure. The surfaces are negatively charged with charge density of one unit charge per $75 \text{ \AA}^2$ the background electrolyte concentration is 0.1 M NaCl . From top to bottom: kinetic pressure $P_{\text{kin}} = \rho_{\text{mid}} k_B T$, sum of all components, hard core contribution P_{core} , short-range ion-ion potential contribution P_{hyd} (dashed line), and electrostatic correlation contribution P_{el} (dotted line).

FIG. 11. An example of short-range ion-ion potential contribution to pressure in the presence of surface adsorption. Oscillatory pressure obtained from short-range part of the potential P_{hyd} (lower curve) leads to oscillations in overall pressure (upper curve). This is the same example as shown in Fig. 6, with surface charge of one unit charge per $135 \text{ \AA}^2$ and 47% compensation of surface charge (well depth $3k_B T$) by adsorbed counterions.

small separations are reached, when it rapidly turns to repulsion. Magnitude of separate components of the pressure (not shown) is very similar to that presented in Fig. 10 for the electrolyte concentration of 0.1 M . However, higher background pressure of the outside electrolyte makes the total net interaction pressure weakly attractive. Attractive double layer pressures in 1:1 electrolytes at high electrolyte concentrations due to a high outside pressure have also been obtained for primitive model electrolytes,²³ but net attractions appears more readily here due to the attractive hydration pressure term.

FIG. 12. Double layer pressure at very high surface charge (full curve with squares). The surfaces are negatively charged with charge density of one unit charge per $48 \text{ \AA}^2$ the background electrolyte concentration is 0.1 M NaCl . With the adsorption of counterions corresponding to 50% (full curve) and 84% (dotted curve) of the surface charge (well depth $2k_B T$ and $4k_B T$, respectively) one finds oscillatory behavior.

FIG. 13. Pressure in 1 M background NaCl electrolyte with the surface charge density of one charge per $75 \text{ \AA}^2$. From top to bottom: PB, primitive model and full aqueous electrolyte.

DISCUSSION

The ionic contribution to the double layer interaction shown in Figs. 5–13 is normally the dominant force between charged surfaces in ionic solutions. It is therefore interesting to consider new features of the interaction found with the present theory that describes ions dissolved in real aqueous solvent. As mentioned earlier, these new effects are important only when surface charge is high (one charge per $135 \text{ \AA}^2$ or higher) and/or counterions adsorb specifically to the surface.

Some effects found in our examples are seen already in the case of featureless inert surfaces that do not specifically interact with dissolved ions (i.e., in absence of the short-range adsorption potential). In this simplest model system the only effect of surface charge is to bring the neutralizing counterions into the space between the walls. We shall discuss this simpler system first.

A general finding is that dense counterion layers that build up near each surface are more compact than calculated using the primitive model.²⁴ This is a consequence of that the ions next to the surface are so many that most of them can assume favorable mutual lateral separations to their neighbors (in the pair potential minima). Furthermore simulations indicate a weak overall attractive contribution that the discrete solvent structure superimposes on the Coulomb force between like-charge ions. We speculate that this average weak attraction is predominantly due to favorable positioning of neighboring water molecules. Water molecules entering the gap between two ions are oriented so that the direct Coulomb repulsion is decreased. This is best seen in images of average charge distribution in the vicinity of the ion pair as obtained in simulation.²⁵

The more compact counterion layers lead to reduced effective surface charge compared to the primitive model, i.e., when viewed from a distance far from the wall, the surface charge density appears significantly diminished. This is normally described as surface adsorption of counterions, which is not an entirely incorrect picture, but the mechanism is very

different from specific ion adsorption. All such charge is not necessarily right at the surface, but also in a more diffuse layer of typical thickness $5\text{--}8 \text{ \AA}$.

At short separations, the ion hydration significantly affects ionic contribution to the double layer pressure. The general behavior here is a weakened repulsion or even attraction in the surface separation range of $6\text{--}12 \text{ \AA}$, and resumption of very strong repulsion at even shorter separations. This later repulsion was previously interpreted as the secondary hydration force. Once we take into account the definition of the separation scale in the present calculation (zero is defined as the state where one layer of counterions remains between the surfaces) the results calculated for surface charge density of about one negative charge per $75 \text{ \AA}^2$ are reminiscent of experimentally measured interaction.^{26,27}

Examination of separate contributions to the pressure shows that the source of increased short-range repulsion between the surfaces is almost entirely the kinetic term P_{kin} . The hydration effect is mostly attractive, and when this is no longer large the normal kinetic repulsion dominates. The strong repulsion is therefore not caused by the “secondary hydration force” but a loss of favorable hydration contribution. Yet the highest pressures measured in the surface force apparatus at separations of only a few $\text{\AA}$ units are not predicted in the present calculation. They may reflect the physical process of the removal of water between the nearest layer of counterions and the surfaces.

An attraction due to hydration effects in about the same separation range as found here has recently been obtained in the work by Otto and Patey,¹⁴ who use effective pair potentials for hydrated ions obtained from a molecular model of dilute solutions. This particular attractive contribution is also present in a model where ion positions are laterally averaged. The attraction obtained at low electrolyte concentrations and high surface charges by Burak and Andelman¹⁰ in a simpler model starting from the average free energy density and using the same $\text{Na}^+ \text{--} \text{Na}^+$ potential shown in Fig. 2 of this work is in qualitative agreement with the aHNC results.

In the second class of examples, we attempted to explore the effect of specific counterion adsorption to simple charged surfaces. Within the McMillan–Mayer theory of nonuniform ionic fluids, this can in principle be done with the same accuracy as achieved in the simpler case of nonadsorbing surfaces. However we did not have the required simulation data for ion–surface potentials in the presence of the solvent, and this part of our study is therefore conducted with the artificial square well potential that does not properly reflect the interaction of a hydrated ion with the surface. Nevertheless, some interesting effects resulted from the available realistic form of the interaction between adsorbed ions (on the same and different surfaces) which was included in the calculation.

The oscillatory interaction pressure found in cases where counterions adsorb strongly to the surface originates from the oscillatory nature of the short-range part of ion–ion interaction. Ultimately, the oscillatory interaction between the surfaces is caused by water structuring between discrete adsorbed ions, and it has the same period as the oscillations measured in the surface force experiment.² This effect is absent (or at least weak) for systems with uniformly charged

surfaces or surfaces where charge is buried in the interior and does not induce a strong hydration shell.

In surface force measurements,² oscillatory interaction was recorded in 1 mM KCl solution, where repulsion in the asymptotic PB regime fits the effective surface potential of -78 mV. Such small value of the effective potential indicates counterion adsorption to the surfaces. In a separate experiment²⁸ in 1 mM LiNO₃ solution Shubin and Kekicheff found strong dependence of the effective potential on the pH value of the solution, indicating that the adsorbing ion is largely H₃O⁺. At pH=10 when H₃O⁺ adsorption is no longer significant and the asymptotic pressure is much stronger.

If the oscillations were due to alkali ions, they should then be present in, e.g., the case of 0.1 M NaCl solutions measured by Pashley and McGuiggan.²⁷ If this is the case, due to the technical limitations of the surface force apparatus measurements²⁹ the oscillations were not observed.

The oscillations must originate from either the adsorbed ions or water ordered at the mica surfaces, where some of the surface charge has been compensated by tightly bound counterions. The oscillatory interaction was previously interpreted² as the effect of solvent layering on mica surfaces. Without the adsorbed counterions, sufficiently strong solvent layering seems unlikely, because water density at an inert van der Waals surface is lower than in the bulk and does not show significant structuring.³⁰ It would therefore appear most likely that oscillations originate from water ordered by tightly adsorbed counterions. The oscillatory effective potential between the ions near one surface with those near the other is reflected in the measured force.

The use of effective potentials between ions in aqueous solutions was advocated many years ago, most notably by Friedman and co-workers.³¹ However, sufficiently accurate simulation studies became available only relatively recently. Bulk properties like activity and osmotic coefficients are correctly described by effective potentials.¹⁶ The investigations reported here made some further steps along the line taken in Refs. 9, 10, 14, and 15. Collectively, these studies show that the use of effective potentials to describe the double layer interaction between charged surfaces is theoretically well founded, with all the required approximations steps known and ready for testing. In practice the method could become an effective and useful tool for studying related problems of increasing complexity.

ACKNOWLEDGMENTS

We are grateful to Professor David Andelman, Professor James Quirk, Professor Richard Pashley, and Professor Sture Nordholm for many valuable discussions. This work has been partly financed by grants from Göteborg University (Mark's Visiting Professorship for S.M.) and the Swedish Natural Science Research Council. S.M. thanks Professor Nordholm for his kind hospitality at the Division of Physical Chemistry, Göteborg University.

APPENDIX

In this appendix we shall derive Eq. (6) for cases where there is a state dependent potential difference $\Delta\psi$ between

the bulk solution and the inhomogeneous system. The intrinsic activity of the inhomogeneous system is $\zeta_s \equiv z_s \exp(-\beta q_s \Delta\psi)$, see main text. The grand partition function of the inhomogeneous system is given by Eq. (2) provided the activities z_s are replaced by the intrinsic activities ζ_s . Alternatively, the same equation is obtained by regarding $\Delta\psi$ as part of the external potential, i.e., taking the total external potential as $V_s(\mathbf{R}) + q_s \Delta\psi$, and then including the $\Delta\psi$ contribution to U_m in the coefficients outside of the integral in Eq. (2) rather than in the integrand.

If one now makes a Taylor expansion in $\boldsymbol{\zeta} = (\zeta_0, \zeta_1, \zeta_2)$ in complete analogy to the expansion in $\mathbf{z}$ referred to in connection with Eq. (3), one can easily derive the analogue of Eq. (3),

$$\begin{aligned} \frac{\Xi(\mathbf{z})}{\Xi(\mathbf{z}^*)} &= \sum_{m_0, m_1, m_2 \geq 0} \frac{1}{m_0! m_1! m_2!} \left(\frac{\zeta_0 - \zeta_0^*}{\gamma_0^*} \right)^{m_0} \\ &\times \left(\frac{\zeta_1 - \zeta_1^*}{\gamma_1^*} \right)^{m_1} \left(\frac{\zeta_2 - \zeta_2^*}{\gamma_2^*} \right)^{m_2} \\ &\times \int \exp[-\beta \tilde{w}^{(\mathbf{m})}(\{\mathbf{R}\}, \mathbf{z}^*)] d\{\mathbf{R}\}, \end{aligned} \quad (\text{A1})$$

where $\zeta_s^* = z_s^* \exp(-\beta q_s \Delta\psi^*)$ and $\tilde{w}^{(\mathbf{m})}$ is obtained from Eq. (4) by substituting $\rho_s^* \rightarrow \tilde{\rho}_s^* \equiv \rho_s^* \exp(-\beta q_s \Delta\psi^*)$ in the rhs. For the solvent we have $\zeta_0 = z_0$ since the solvent molecules have no net charge.

To obtain the analogue of Eq. (5) we would need to make $\zeta_s^* = 0$ for all $s \neq 0$. As we have seen, it is in general not sufficient to let $z_s^* \rightarrow 0$ for all $s \neq 0$ since for counterions $\zeta_s^* \neq 0$ in this limit for the geometries in question. To accomplish our task we instead introduce an inhomogeneous reference system with a different external potential. We assume that this system is in equilibrium with the same bulk solution of specified activities as our original system. Furthermore, we require that the electrostatic part of the external potential in this system originates from an external charge distribution with zero net charge. Thereby, the problem above does not arise for this system; there are no counterions that have to remain there to ensure electroneutrality.

If the external electrostatic potential of the reference system differs only by a constant χ from that of our original system, we can, in fact, calculate $\Xi(\mathbf{z})$ from a Taylor expansion in $\mathbf{z}$ for the reference system by using an argument analogous to that we used above to obtain Eq. (5) from Eq. (2). In planar geometry we can obtain such a reference system from our original system by adding two equal, planar and uniform surface charge distributions, each with a surface charge density $\sigma^\dagger$ as discussed in the main text. The original system is placed between these sheets of surface charge, where the potential from them is constant. To make the net external charge of the reference system equal to zero, $-2\sigma^\dagger$ must be equal to the total external charge per unit area of our original system.

For the reference system Eq. (A1) applies and gives $\Xi^\dagger(\mathbf{z})/\Xi^\dagger(\mathbf{z}^*)$ expressed in terms of $\zeta_s^\dagger$, $\zeta_s^{\dagger*}$, and $\tilde{w}^{\dagger(\mathbf{m})}$, where dagger (†) implies "reference system." Since the reference and original systems differ only by the constant potential χ we will obtain $\Xi(\mathbf{z})$ instead of $\Xi^\dagger(\mathbf{z})$ by substitut-

ing $\zeta_s^\dagger \rightarrow \zeta_s \exp(\beta q_s \chi)$ in this equation (this amounts to the evaluation of the Taylor expansion of $\Xi^\dagger$ at a different set of activities ζ). If we now let $z_s^* \rightarrow 0$ for all $s \neq 0$ we have $\zeta_s^{\dagger*} \rightarrow 0$ and obtain

$$\begin{aligned} \frac{\Xi(\mathbf{z})}{\Xi^\dagger(z_0, 0, 0)} &= \sum_{\substack{m_1, m_2 \geq 0 \\ m_0 = 0}} \frac{1}{m_1! m_2!} \left(\frac{\zeta_1 \exp(\beta q_1 \chi)}{\gamma_1^0} \right)^{m_1} \\ &\quad \times \left(\frac{\zeta_2 \exp(\beta q_2 \chi)}{\gamma_2^0} \right)^{m_2} \\ &\quad \times \int \exp[-\beta \tilde{w}^\dagger(\mathbf{m})(\{\mathbf{R}\}, z_0, 0, 0)] d\{\mathbf{R}\}. \end{aligned} \quad (\text{A2})$$

To write this in a similar form as Eq. (5) we introduce the difference $\Delta\Psi$ in the constant part of the external electrostatic potentials of the two systems

$$\Delta\Psi = \Delta\psi(\mathbf{z}) - \chi - \Delta\psi^\dagger(z_0, 0, 0), \quad (\text{A3})$$

where $\Delta\psi(\mathbf{z})$ is the potential difference between bulk and the original inhomogeneous system at activities $\mathbf{z}$ and $\Delta\psi^\dagger(z_0, 0, 0)$ is the corresponding quantity for the reference system at activities $(z_0, 0, 0)$. Equation (A2) now yields Eq. (6) which is the final result.

¹J. N. Israelachvili and H. Wennerström, *Nature (London)* **379**, 219 (1996).

²R. M. Pashley and J. N. Israelachvili, *J. Colloid Interface Sci.* **101**, 511 (1984).

³See, e.g., E. Guàrdia, R. Rey, and J. A. Padró, *J. Chem. Phys.* **95**, 2823 (1991); D. E. Smith and L. X. Dang, *ibid.* **100**, 3757 (1994).

⁴S. A. Adelman, *Chem. Phys. Lett.* **38**, 567 (1976).

⁵S. A. Adelman, *J. Chem. Phys.* **64**, 724 (1976).

⁶A. P. Lyubartsev and A. Laaksonen, *Phys. Rev. E* **52**, 3730 (1995).

⁷H. L. Friedman, *J. Chem. Phys.* **76**, 1092 (1982).

⁸J. S. Høye and G. Stell, *J. Chem. Phys.* **102**, 2841 (1995).

⁹S. Marčelja, *Nature (London)* **385**, 689 (1997).

¹⁰Y. Burak and D. Andelman, *Phys. Rev. E* **62**, 5296 (2000); *J. Chem. Phys.* **114**, 3271 (2001).

¹¹R. Kjellander and S. Marčelja, *J. Chem. Phys.* **82**, 2122 (1985).

¹²J. E. Mayer, *Equilibrium Statistical Mechanics* (Pergamon, Oxford, 1968).

¹³T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).

¹⁴F. Otto and G. N. Patey, *J. Chem. Phys.* **112**, 8939 (2000).

¹⁵S. Marčelja, *Langmuir* **16**, 6081 (2000).

¹⁶P. Lyubartsev and A. Laaksonen, *Phys. Rev. E* **55**, 5689 (1997).

¹⁷R. Pottel, in *Water—A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1973), Vol. 3, pp. 418–422.

¹⁸J. Anderson, J. Ulo, and S. Yip, *J. Chem. Phys.* **87**, 1726 (1987).

¹⁹A. P. Lyubartsev and A. Laaksonen, *J. Chem. Phys.* **111**, 11207 (1999).

²⁰G. Sposito, N. T. Skipper, R. Sutton, S. Park, A. Soper, and J. A. Great-house, *Proc. Natl. Acad. Sci. U.S.A.* **96**, 3358 (1999).

²¹R. Kjellander and S. Marčelja, *Chem. Phys. Lett.* **127**, 402 (1986).

²²Due to an error in a conversion factor, this feature was missed in earlier reports by one of us (Refs. 9 and 24) where short-range potential contribution to ionic pressure P_{hyd} was presented as negligibly small. We regret the inconvenience this error has caused.

²³H. Greberg, R. Kjellander, and T. Åkesson, *Mol. Phys.* **92**, 35 (1997).

²⁴S. Marčelja, *Periodicum Biologorum* **100**, Suppl 2, 7 (1998).

²⁵See images by A. Lyubartsev at <http://www.fos.su.se/physical/sasha/shells/hydro.html>

²⁶R. M. Pashley, *J. Colloid Interface Sci.* **83**, 531 (1981).

²⁷P. M. McGuiggan and R. M. Pashley, *J. Phys. Chem.* **92**, 1235 (1988).

²⁸V. E. Shubin and P. Kekicheff, *J. Colloid Interface Sci.* **155**, 108 (1993).

²⁹R. M. Pashley (private communication). Strong repulsion at 0.1 M NaCl leads to surfaces jumping to large separation on the outward run of the apparatus.

³⁰E. Spohr, *J. Chem. Phys.* **106**, 388 (1997).

³¹For example, E. C. Zhong and H. L. Friedman, *J. Phys. Chem.* **92**, 1685 (1988).