

Osmotic interactions between neutral surfaces in an electrolyte solution

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Osmotic forces between planar interfaces with intervening electrolyte solution are studied by means of a Monte Carlo simulation with a two-dimensional Ewald summation. A short-ranged, usually attractive, interaction is observed in solutions dominated by electrostatic correlations among the ions. At higher concentrations, the Coulombic interactions compete with packing effects that give rise to an oscillatory interaction similar to the structural forces frequently observed between colloidal particles in dense fluids. The osmotic force in vanishingly narrow pores obeys the exact limiting law that relates the pressure on the walls to the fugacity and to the osmotic pressure of the external solution.

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I. INTRODUCTION

In recent years forces between colloidal surfaces have represented a major focus of experimental and theoretical research [1-3]. In view of their importance for the stability of colloidal dispersions, theories of interacting double layers have enjoyed particular attention. Classical mean-field approaches [3,4] were supplemented by modern integral equation theories [5-9] and computer simulations [10-18]. The accuracy of these novel methods allowed studies of complex situations characterized by a sensitive balance of various effects. In systems where ion-ion correlations have a pronounced role, this has led to new interpretations of double-layer interactions in colloidal systems. Both analytic theories and simulations have revealed the existence of a notable attractive contribution to the overall force between electric double layers. This leads to a reduced repulsion or, in extreme cases, typically in the presence of multivalent counterions, even to a weak attraction between equally charged surfaces [5,10]. An analogous mechanism has been found to affect the interactions among spherical [13] or cylindrical [19] polyions and between aqueous droplets in microemulsions [20,21]. The common feature of these systems was the presence of charged surfaces and neutralizing counterions distributed throughout the electric double layer next to the interface. The ion-ion correlation effects considered in the above cases, are, however, not limited to the situations involving the presence of electrified surfaces or charged macroparticles [16,22,23]. In the present paper, we present simulation results for the osmotic forces between neutral surfaces with intervening electrolyte solutions. The effect of the correlations among the ions on their distribution next to the surface is considered, and the concomitant osmotic force between neutral walls is determined in a number of systems. The

existence of this kind of force has been indicated in our previous work where the exact limiting law for ion distribution in vanishingly narrow slits has been established [22]. This result has been confirmed in a simulation study by Valleau, Ivkov, and Torrie [16], who considered the pressure between the plates in a concentrated divalent salt solution. It is, however, of interest to explore the effect more systematically and in a broader range of conditions. In addition, we are concerned with the effects of longer-ranged periodic boundary conditions. In the above study [16], mainly dealing with charged surfaces, the long-ranged interactions along the walls were treated within the mean-field approximation. While capturing the contribution of the charge-density profile outside the simulation cell, the method does not account for ion-ion correlations beyond the range determined by the minimum-image convention. It is therefore desirable to extend these calculations by using the essentially infinite Ewald summation along lateral directions. The width dependence of the pressure on the plates is studied using a simple model consisting of smooth interfaces and the primitive model of ionic solution [24]. The structure of the solution between the walls in equilibrium with the bulk phase of prescribed concentration and chemical potential of the salt is determined by Monte Carlo simulation. The dependence of the ion distribution next to the surfaces on the distance between them determines the net osmotic force between the two plates as a function of the separation. The resulting interaction between the walls is usually found to be attractive, short ranged, and of a magnitude comparable to the attractive components of the net forces between electrified surfaces seen in earlier works [5,10]. As found in a preceding study [22], the net interaction at very small separation between the two surfaces obeys the limiting expression for ion adsorption which relates the force between the plates to thermodynamic properties of the solution [22,23].

II. MODEL AND METHOD

The model we use consists of two parallel, semi-infinite plates immersed in an electrolyte solution [22]. The latter is represented by the restricted primitive model RPM [24] in which the ions behave as hard spheres of charge $\pm Ze_0$ and of diameter σ embedded in a dielectric background of permittivity ϵ . Ignoring possible image effects [12], a uniform permittivity is assumed throughout the system. The configuration-dependent part of the Hamiltonian consists of ion-ion (u_{ij}) and ion-wall (u_{iw}) interactions:

$$U = \sum_i \sum_j u_{ij}(r_{ij}) + \sum_i u_{iw}(z_i),$$

$$u_{ij}(r_{ij}) = \begin{cases} \infty & \text{if } r_{ij} < \sigma \\ Z_i Z_j e_0^2 / 4\pi\epsilon r_{ij} & \text{otherwise,} \end{cases} \quad (1)$$

$$u_{iw}(z_i) = \begin{cases} \infty & \text{if } |z_i| > L/2 \\ 0 & \text{if } |z_i| < L/2, \end{cases}$$

where $L + \sigma$ is the separation between the two surfaces, z_i is the coordinate of ion i normal to the plates, and $z_i = 0$ corresponds to the midplane between the walls. The plates are perfectly smooth and sufficiently thick, so we can neglect any correlations across the walls. For a purely hard-core interaction between the ions and the walls, the osmotic pressure is determined by the contact number density of the ions ρ_c . The total force F per unit area S of a plate corresponds to the difference between the pressures exerted on the inner and outer surfaces of the plates [25]:

$$F/S = P_{\text{in}} - P_{\text{out}} = [\rho_c(L) - \rho_c(\infty)]kT. \quad (2)$$

The pressure exerted at the outer surfaces of the plates $P_{\text{out}} = \rho_c(\text{out})kT = \rho_c(\infty)kT$ equals the osmotic pressure of the solution $\Pi = \phi\rho_b kT$, where ρ_b is the mean number density of the ions in the bulk phase, and ϕ is the osmotic coefficient of the solution. For very narrow pores, the ion density has been shown [22] to approach a well-defined limiting value

$$\lim_{L \rightarrow 0} \rho = f_{\pm} = \gamma_{\pm} \rho_b, \quad (3)$$

where f_{\pm} is the fugacity and γ_{\pm} the mean activity coefficient of the ions. At separations $L \ll \sigma$, the liquid density in the pore becomes practically uniform, the contact density ρ_c approaching the average density in the pore. The force between the plates at a separation $L + \sigma$ barely exceeding the thickness of a monolayer of adsorbed ions σ can therefore be expressed as [22,23]

$$\lim_{L \rightarrow 0} F/S = [\lim_{L \rightarrow 0} \rho_c - \rho_c(\infty)]kT = [\gamma_{\pm}/\phi - 1]\Pi, \quad (4)$$

i.e., the force per unit area is proportional to the

difference $\gamma_{\pm} - \phi$ times the ideal osmotic pressure of the solution. The osmotic coefficient ϕ normally exceeds γ_{\pm} giving rise to the attraction between adjacent plates. If the walls get even closer, i.e. for $-\sigma \leq L \leq 0$, all ions are squeezed from the slit, $\rho_c(\text{in}) = 0$, and the net force per area becomes oppositely equal to the osmotic pressure of external solution.

At finite separations L , the average concentration and the contact density of the ions at the walls are functions of the separation between the plates [16,22,23]. In the present work, the contact number densities ρ_c for different separations are obtained by extrapolation to $z = \pm L/2$ of the simulation results for the mean density $\rho_{\pm}(z)$ in the slices obtained by dividing the simulation cell by a set of equidistant planes parallel to the plates. The average number density of the ions in narrow pores is generally quite different from that of the bulk solution [16,22,23,26–29]. In an earlier work, we studied the overall distribution of the ions between the pore and the bulk solution by a grand-canonical ensemble Monte Carlo simulation (GCMC) [22]. The convergence in the overall number of the ions in wide pores was found to be much faster than the convergence of the detailed ion density profiles in the gap. The average densities of the ions determined [22] by GCMC at specific plate separations were therefore used to obtain accurate wall-ion contact densities by means of the canonical ensemble simulation (CMC). The GCMC profiles from Ref. [22] for gap widths below about a fifth of the ionic diameter were sufficiently smooth to be used without further CMC calculation.

The effects studied in this and the preceding work are most pronounced in narrow pores where screening effects are weaker [30–32] than in the corresponding bulk solutions. The accuracy of the simulation may therefore depend on the appropriate account of long-ranged correlations. To reduce the effects of the finite size of the simulation cell, the periodic boundary conditions [33] were applied along the lateral directions x and y . The planar slit of width L was treated as a two-dimensional array of equal, periodically repeating cells [34–37] of volume $V = L_{xy}^2 L$ with identical configurations of mobile ions. The potential energy of a cell containing N ions was calculated according to the relation [33]

$$U_N = \sum_{i=1}^N \sum_{j=1}^N \sum_{\mathbf{P}} Z_i Z_j e_0^2 / 8\pi\epsilon |\mathbf{r}_{ij} + \mathbf{P}|. \quad (5)$$

The sum over lattice vectors \mathbf{P} includes the points $\mathbf{P} = (lL_{xy}, mL_{xy}, 0)$, where m and l are integers running from zero to infinity and the self-term $i = j$ is omitted in the basic cell $l = m = 0$. The infinite sum over \mathbf{P} is calculated by Ewald's method adapted to two-dimensional periodic conditions [34,35]. This entails the application of the relations.

$$U_N = \frac{1}{2} \sum_{i=1}^N \left\{ \sum_{j=1}^N [u_{ij}^{(1)}(\mathbf{R}_{ij}) + u_{ij}^{(2)}(\mathbf{R}_{ij}) + u_{ij}^{(3)}(\mathbf{R}_{ij})] + u_i^{(4)} \right\}, \quad (6)$$

$$u_{ij}^{(1)}(\mathbf{R}_{ij}) = (Z_i Z_j e_0^2 / 4\pi\epsilon) \sum_{\mathbf{P}} \text{erfc}(-\kappa R_{ij}) / R_{ij}, \quad (7)$$

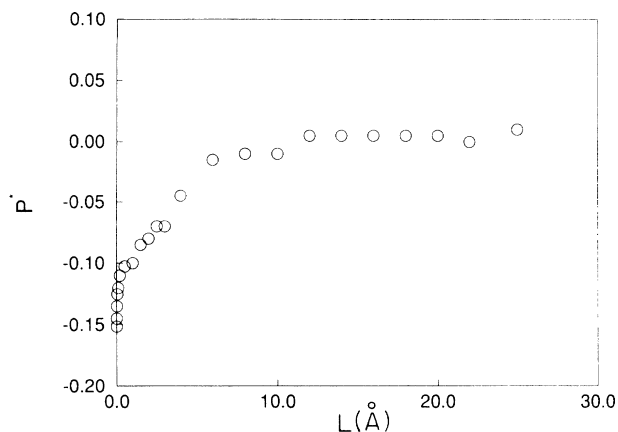


FIG. 1. The reduced pressure $P^* = F/(S\rho_b kT)$ between neutral plates immersed in 0.1-mol dm⁻³ solution of a monovalent electrolyte as a function of the distance between the plates L .

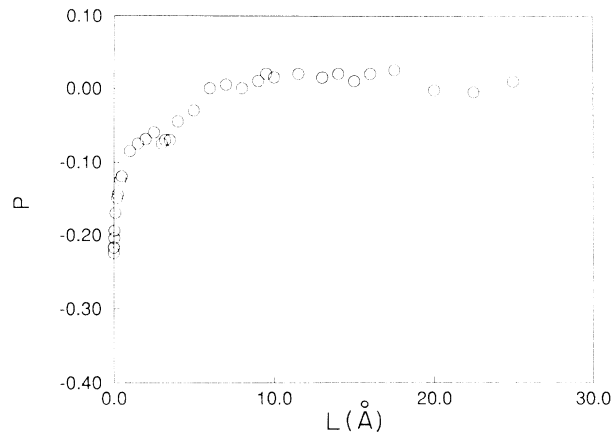


FIG. 2. The reduced pressure P^* between neutral plates immersed in 1.001-mol dm⁻³ solution of a monovalent electrolyte as a function of the distance L .

$$u_{ij}^{(2)}(\mathbf{R}_{ij}) = (\mathbf{Z}_i \mathbf{Z}_j e_0^2 / 4\pi\epsilon L_{xy}^2) \sum_{k=0} \exp(i\mathbf{k}\mathbf{r}_{ij}) / k [\exp(k|z_{ij}|) \operatorname{erfc}(k/2\kappa + \kappa|z_{ij}|) + \exp(-k|z_{ij}|) \operatorname{erfc}(k/2\kappa - \kappa|z_{ij}|)] , \quad (8)$$

$$u_{ij}^{(3)}(\mathbf{R}_{ij}) = -(\mathbf{Z}_i \mathbf{Z}_j e_0^2 / 2\pi\epsilon L_{xy}^2) [z_{ij} \operatorname{erf}(\kappa z_{ij}) + \exp(-\kappa^2 z_{ij}^2) / (\pi^{1/2} \epsilon)] , \quad (9)$$

$$u_i^{(4)} = -\mathbf{Z}_i^2 e_0^2 \kappa / 2\pi^{1/2} . \quad (10)$$

Above, $\mathbf{R}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $R_{ij} = |\mathbf{R}_{ij}|$, \mathbf{k}_{ij} is the two-dimensional reciprocal-lattice vector, $k_{ij} = |\mathbf{k}_{ij}|$, $\mathbf{r}_{ij} = (x_{ij}, y_{ij})$, $z_{ij} = z_i - z_j$, and κ is the screening parameter of the Gaussian distributions introduced in Ewald method [33]. Apart from the use of the closed (N, V, T) ensemble, with the numbers of ions N taken from earlier GCMC simulation of the same systems, the details of the calculation were as described in the preceding work [22]. The dimensions of the Monte Carlo cell were adjusted to accommodate between 50–100 simple ions, along with the condition that the xy size always exceed the width of the slit. The maximum displacement of the ions was chosen in such a way that we maintained about 40–50% acceptance of attempted moves in the simulation. 56 k -space vectors were used in the two-dimensional Ewald summation. This would correspond to about 3×10^2 vectors in a three-dimensional system. About 5×10^4 moves were attempted during the equilibration, and $(2.5\text{--}5) \times 10^5$ moves were made during the averaging procedure to obtain an estimated accuracy in the density profiles of about $\pm (1.0\text{--}2.5)\%$. Effects of the system size

and the Ewald sum parameters have been carefully explored in the preceding GCMC study of the same systems [22].

III. RESULTS AND DISCUSSION

The system parameters used in the present calculations are taken from earlier simulation studies of bulk [38,39] and confined [16,22] restricted primitive model (RPM) electrolytes. The systems considered comprise monovalent and divalent symmetric electrolytes at different concentrations, listed in Table I where known [16,38–40] thermodynamic coefficients of bulk solutions are also included. All the data correspond to the temperature $T = 298$ K and relative permittivity $\epsilon_r = 78.5$. In the last two columns, we give the limiting values of the reduced pressure $P^* = F/(S\rho_b kT)$ between the walls at vanishing separation L determined by Eq. (4) and from the simulation [22]. At distances $-\sigma \leq L \leq 0$, the reduced pressure P^* equals -1.0 . The L dependence of P^* at finite separations is illustrated in Figs. 1–5. The limiting values

TABLE I. The properties of RPM electrolytes considered in the simulations.

System	Valency	σ (nm)	c (mol dm ⁻³)	ϕ	$\ln \gamma_{\pm}$	P^*	
						Eq. (4)	MC
1	1:1	0.425	0.1031	0.9451	-0.2311	-0.1514	-0.1521
2	1:1	0.425	1.001	1.094	-0.1165	-0.2128	-0.2245
3	1:1	0.425	1.968	1.346	0.2545	-0.0562	-0.0540
4	2:2	0.420	0.0456	0.650	-1.437	-0.4024	-0.4057
5	2:2	0.420	0.971	0.651	-2.635	-0.579	-0.583

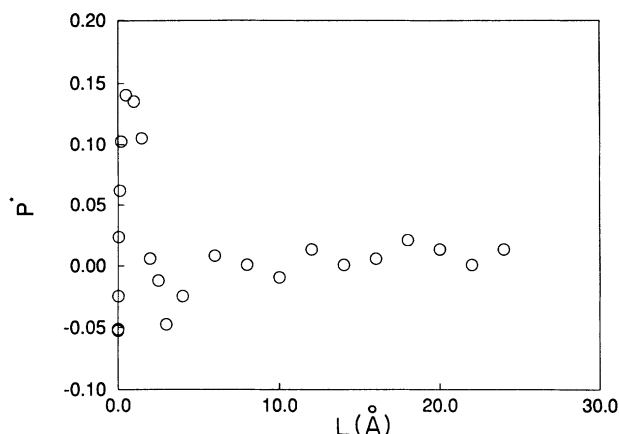


FIG. 3. The reduced pressure P^* between neutral plates immersed in a 1.968-mol dm^{-3} solution of a monovalent electrolyte as a function of the separation between the plates L .

$P^*(0)$ practically coincide with the prediction of the exact relation, Eq. (4) [22]. Negative values of $P^*(0)$ reveal the presence of an attractive osmotic force between adjacent surfaces immersed in the solution. The reduced density of the ions in the slit, and the concomitant reduction in the pressure on the walls, stem from the tendency of the ions to avoid the region where their ionic atmosphere is distorted by the presence of the walls. At higher concentrations, the packing effects contribute in the opposite direction. In monovalent salt solutions, the calculated force rapidly decays from the limiting value over a distance equal to a small fraction of the diameter of the ions. This rapid decay is not observed in the presence of divalent salt. At somewhat larger separations, the force decay is slowed down, but qualitatively different pictures emerge at different conditions. In dilute solutions of monovalent electrolyte and in both systems with divalent ions, the ion-ion correlations appear to be dominated by electrostatic effects that give rise to a monotonical weakening of the osmotic force with the distance between the walls. The range of the force extends over a wall-wall distance of several ionic diameters, and appears to increase with the valency of the ions. The results for the

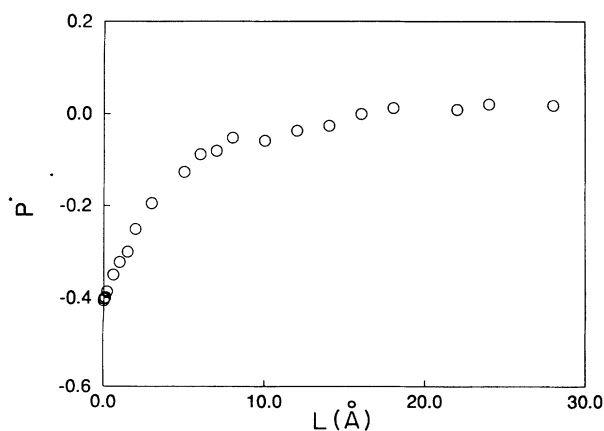


FIG. 4. The reduced pressure P^* between neutral plates in a $0.0456\text{-mol dm}^{-3}$ solution of a divalent electrolyte as a function of the wall-wall separation L .

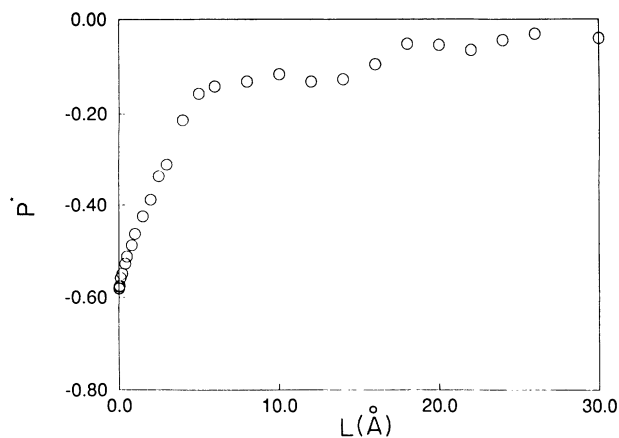


FIG. 5. The reduced pressure P^* between neutral plates immersed in a 0.971-mol dm^{-3} solution of a divalent electrolyte as a function of the wall-wall separation L .

concentrated divalent electrolyte, system 5, appear to be in good agreement with previous work [16], although we observe a somewhat longer range of wall-wall attraction. In highly concentrated solutions such as system 3 depicted in Fig. 3, the ion-ion correlations are apparently dominated by packing effects, as is expected from the values of thermodynamic coefficients listed in Table I. The osmotic force shown in Fig. 3 is therefore reminiscent of what has been seen in studies of structural forces in dense molecular fluids [25,41–47] confined by planar interfaces. While simulations reveal the existence of a nonspecific osmotic contribution to the interaction between neutral interfaces, the effect appears to be weaker than some of the measured salt effects between apolar surfaces in aqueous solutions [1–3]. The present results correspond to the sole contribution of the ion-ion correlations, and can be useful as a benchmark for approximate theories such as those discussed in Ref. [23]. In real systems, the presence of a simple electrolyte has often been found to alter the strength of surface forces in both the short- and long-ranged regimes [1,2]. At least part of these effects should be attributed to more specific ion-surface interactions. These would include the screening of existing polar groups, or the adsorption of the ions that could give rise to or alter the existing surface charge on the particles. The present model with pure hard-core ion-wall interaction cannot capture these contributions. Introduction of specific ion-wall attraction in a tractable form of Baxter's adhesion is currently under consideration. The presence of the electrolyte may also be felt through its interactions with the molecules of the solvent. These interactions can lead to highly specific effects that should be considered within the framework of nonprimitive models for an electrical double layer [48,49] to be considered at a later date.

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