

Influence of Interionic Correlations on the Free Energy of Charged Interfaces: A Direct Derivation from (*N,V,T*) Monte Carlo Simulations

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The stability of charged interfaces varies as a function of the nature of their neutralizing counterions. Changing the counterions from monovalent to divalent cations enhances the interionic correlations and drastically reduces the strong interfacial repulsion, leading, in some cases, to a net attraction. We have used Monte Carlo simulations in the canonical ensemble in order to obtain a direct derivation of the free energy of two charged lamellae, including the contribution of the interionic correlations in the derivations of the interfacial energy and entropy. This interfacial free energy may be used as an effective potential describing the stability of such charged interfaces without requiring the knowledge of the counterion distribution at the solid/liquid interfaces. This procedure is validated by an independent derivation of the net interfacial pressure.

I. Introduction

Colloids are materials involved in many industrial applications (water treatment, waste management, drilling fluids, paint, food and cosmetic industry, etc.) because of their various physico-chemical properties (high specific surface and absorbing power, ionic exchange capacity, gelling, thixotropy, etc.). In contrast with neutral colloids, the long-range interactions between charged colloids are monitored by the overlap between their diffuse layers of counterions. The behavior of such charged colloids neutralized by monovalent counterions and dispersed in water is well described by a simplified model (like the DLVO^{1,2} theory derived from a numerical solution of the Poisson–Boltzmann equation³) because the interionic correlations remain negligible. However, when the strength of the ion/colloid electrostatic coupling increases, i.e., by increasing the valency of the counterions^{4–9} or decreasing the dielectric constant of the solvent,⁸ interionic correlations becomes important and a reliable prediction of the behavior of such colloidal dispersions requires a complete treatment of the electrostatic coupling between the charged particles and their surrounding ions. As an example, Monte Carlo simulations are required to predict quantitatively how the swelling behavior reported for aqueous dispersions of charged colloids neutralized by monovalent counterions progressively switches⁹ to a cohesive behavior when divalent counterions are gradually introduced into the dispersion.

In that context, we have derived from Monte Carlo simulations¹⁰ a direct derivation of the interfacial free energy which may be used as an empirical interparticle potential^{11,12} useful to describe the stability of such charged colloids as a function of their separation and relative orientation, without requiring a detailed analysis of the distribution of their numerous neutralizing counterions. This approach was restricted to the case of monovalent counterions because our derivation of the interfacial entropy was based simply on the mixing entropy which totally neglects the contribution of the interionic correlations. In the present approach, the contribution of the interionic correlation

is explicitly introduced in the derivation of the interfacial entropy, extending the validity of our approach to the case of charged interfaces neutralized by divalent counterions. The validity of this procedure is carefully examined by comparing the variation of the interfacial free energy as a function of the interlamellar separation, either calculated by (*N,V,T*) Monte Carlo simulations or analytically integrated from the empirical law fitted on the calculated interfacial pressure.

II. Methods

A. Electrostatic Energy. The (*N,V,T*) Monte Carlo simulations are performed for two infinite charged lamellae (thickness 10 Å) immersed in a large simulation cell (length 830 Å, width 800 Å). The 6272 monovalent electric charges of the lamellae are distributed in two squared networks, each located at 2.5 Å from the basal surfaces of the lamellae (see Figure 1). The average surface density of the lamellae is thus $4.9 \times 10^{-3} \text{ e/Å}^2$, i.e., the order of magnitude of the surface charge density of various metallic oxides,¹³ including clay minerals.¹⁴ In the framework of the primitive model,¹⁵ the interactions between the solvated ions are described by

$$u(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}}, \quad \text{if } r_{ij} \geq a_i + a_j \quad (1a)$$

$$u(r_{ij}) = \infty, \quad \text{elsewhere} \quad (1b)$$

where a_i is the ionic radius. Our simulations were performed with radii equal to 2.125 and 2.5 Å to mimic hydrated sodium and calcium counterions¹⁶ respectively.

Ewald summation¹⁷ is used in addition with the minimum image convention¹⁰ in order to calculate the electrostatic energy of the interfaces, by summing the repulsive (lamella/lamella and

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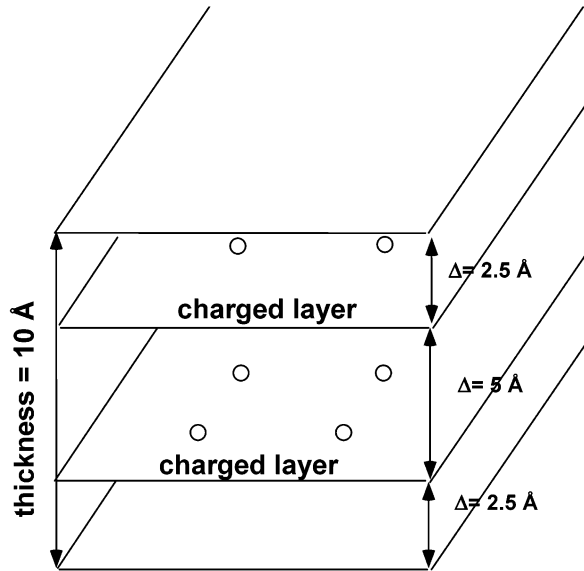


Figure 1. Illustration of the two networks of charged sites distributed within each lamella.

ion/ion) and attractive (ion/lamella) electrostatic contributions:

$$E_{\text{elect}} = E_{\text{dir}} + E_{\text{rec}} + E_{\text{self}} \quad (2a)$$

$$E_{\text{dir}} = \frac{1}{8\pi\epsilon_0\epsilon_r} \sum_{i=1}^{N_i} q_i \sum_{j=1, i \neq j}^{N_j} \frac{q_j \text{erfc}(\alpha r_{ij})}{r_{ij}} \quad (2b)$$

$$E_{\text{rec}} = \frac{1}{2V\epsilon_0\epsilon_r} \sum_{\vec{K} \neq 0} \frac{\exp(-|\vec{K}|^2/4\alpha^2)}{|\vec{K}|^2} [\{\sum_i q_i \cos(\vec{K} \times \vec{r}_i)\}^2 + \{\sum_j q_j \sin(\vec{K} \times \vec{r}_j)\}^2] \quad (2c)$$

$$E_{\text{self}} = \frac{-\alpha}{4\pi^{3/2}\epsilon_0\epsilon_r} \sum_i q_i^2 - \frac{1}{8\pi\epsilon_0\epsilon_r\alpha} \sum_{i=1}^{n_a} q_i \sum_{j=1, j \neq i}^{n_a} \frac{q_j \text{erf}(\alpha r_{ij,\alpha})}{r_{ij,\alpha}} \quad (2d)$$

where the second term of eq 2d is evaluated for the set of electric charges located on the same lamella. The simulations were performed with $\alpha = 7.5 \times 10^{-3} \text{ \AA}^{-1}$ and with 2196 replicas in the reciprocal space summation, leading to an estimate of the electrostatic energy with an accuracy better than 0.003.¹⁸ The temperature was taken to be 298 K for salt-free suspensions.

B. Net Interlamellar Pressure. The interlamellar pressure is also derived from the results of the (N,V,T) Monte Carlo simulations, by dividing the net force acting on the lamellae by their cross section. In the framework of the primitive model,¹⁵ the force acting of the lamellae results from the electrostatic (lamella/lamella repulsion and ion/lamella attraction) and the contact ion/lamella contributions. Ewald summation is also used to derive the electrostatic contribution to the force:¹⁷

$$\vec{F}_{\text{el}}^{\text{dir}} = \sum_{i \in p} q_i \sum_{j \in p} q_j \left[\frac{2\alpha r_{ij} \exp(-\alpha^2 r_{ij}^2) + \sqrt{\pi} \text{erfc}(\alpha r_{ij})}{4\pi^{3/2}\epsilon_0\epsilon_r} \right] \frac{\vec{r}_{ij}}{r_{ij}^3} \quad (3a)$$

$$\vec{F}_{\text{el}}^{\text{rec}} = \frac{-1}{\epsilon_0\epsilon_r V} \sum_{i \in p} q_i \sum_{\vec{K} \neq 0} \frac{\vec{K} \exp(-|\vec{K}|^2/4\alpha^2)}{|\vec{K}|^2} \sum_j q_j \sin(\vec{K} \times \vec{r}_{ij}) \quad (3b)$$

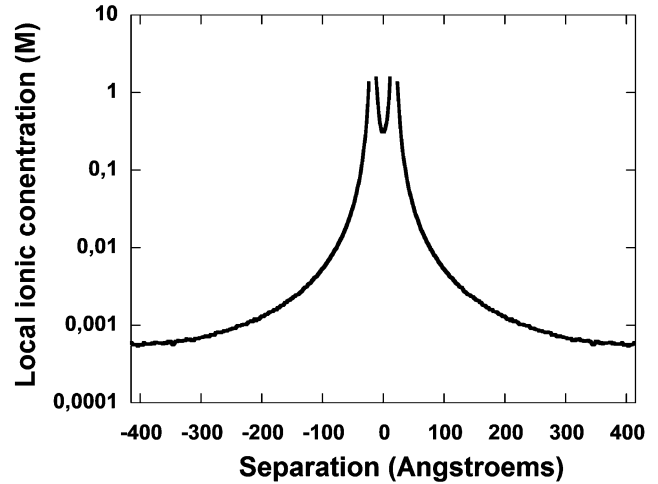


Figure 2. Average ionic concentration profiles of the sodium counterions condensed in the inner and outer domains limited by two charged lamellae with a period of 35 Å.

The contact repulsion is evaluated from the ionic concentration profiles (see Figure 2) describing the distribution of the counterions between the lamellae and outside the interlamellar domains:

$$P_{\text{cont}} = \frac{kT}{S} \int_{\text{surf}} (c_i^{\text{intra}}(0) - c_i^{\text{extra}}(0)) ds \quad (4)$$

where S is the cross section of the lamellae, $c_i^{\text{intra}}(0)$ and $c_i^{\text{extra}}(0)$ the ionic densities in contact with the lamellae, respectively, in the intralamellar and outer-lamellar domains. Since the maximum interlamellar separation is 100 Å (see Figure 4), the contact densities in the outer-lamellar domain is not sensitive to the overlap between their diffuse layers of counterions. Because of the ionic condensation phenomenon, the local densities of the counterions vary steeply near the charged lamellae (see Figure 2). The contact densities used in eq 4 are thus extrapolated by fitting the ionic densities on a quadratic law by using a set of five separations ranging between 0.1 and 0.5 Å. Since these separations are smaller than the ionic radius, this procedure was shown to lead to reliable results.^{8-9,11-12}

C. Direct Derivation of the Entropy. As shown many years ago,¹⁹⁻²¹ interionic correlations may be explicitly introduced in the derivation of the interfacial entropy by using the distribution functions of the labile ions. For heterogeneous systems, this derivation leads to the multiparticle correlation expansion:²²

$$S = S^{(1)} + S^{(2)} + S^{(3)} + \dots \quad (5a)$$

$$S^{(1)} = -k\rho_0 \int P(\vec{x}_1) \ln[P(\vec{x}_1)] d\vec{x}_1 \quad (5b)$$

$$S^{(2)} = -\frac{k\rho_0^2}{2} \int P(\vec{x}_1) d\vec{x}_1 \int P(\vec{x}_2) g_2(\vec{x}_1, \vec{x}_2) \ln[g_2(\vec{x}_1, \vec{x}_2)] d\vec{x}_2 \quad (5c)$$

$$S^{(3)} = -\frac{k\rho_0^3}{6} \int P(\vec{x}_1) d\vec{x}_1 \int P(\vec{x}_2) d\vec{x}_2 \int P(\vec{x}_3) d\vec{x}_3 \times \left(g_3(\vec{x}_1, \vec{x}_2, \vec{x}_3) \ln \left[\frac{g_3(\vec{x}_1, \vec{x}_2, \vec{x}_3)}{g_2(\vec{x}_1, \vec{x}_2)g_2(\vec{x}_1, \vec{x}_3)g_2(\vec{x}_2, \vec{x}_3)} \right] - g_3(\vec{x}_1, \vec{x}_2, \vec{x}_3) + 3g_2(\vec{x}_1, \vec{x}_2)g_2(\vec{x}_1, \vec{x}_3) - 3g_2(\vec{x}_1, \vec{x}_2) + 1 \right) \quad (5d)$$

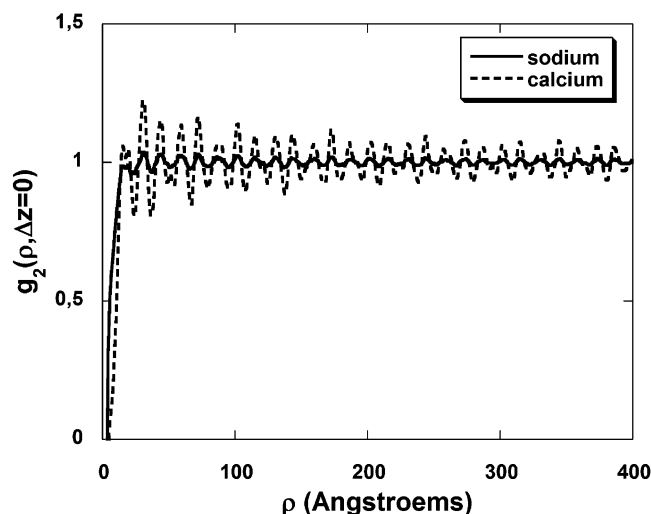


Figure 3. Radial distribution functions illustrating the interionic correlations within the layers of sodium and calcium cations condensed at contact with the charged lamellae in the interlamellar domain (see text).

where $P(\vec{x}) = \rho(\vec{x})/\rho_0$, $\rho(\vec{x})$ is the local ionic density, and ρ_0 is the average ionic density.

Equation 5b is the first-order contribution, simply describing the mixing entropy previously introduced in our derivation of the free energy.^{11–12} To reproduce the steep variations of the ionic density near the charged surfaces, the mixing entropy is evaluated by dividing the interlamellar and outer-lamellar domains in two symmetrical subunits, each limited by its proximal lamellar surface. Each subunit is divided in three sets of parallel shells with a thickness increasing as a function of their separation from the lamella surface (five shells with a thickness of 0.6 Å near the lamella, then five shells with a thickness 3 Å at larger separations, and finally 80 shells with a thickness of 10 Å for the remaining space). The local ionic density within each shell is evaluated by further dividing the shells into nonoverlapping boxes (width 2 Å for the first set, 4 Å for the second, and 10 Å for the last).

Equation 5c describes the second-order contribution to the interfacial entropy; it explicitly includes the first contribution from the interionic correlation. The pair distribution functions g_2 are evaluated by exploiting the cylindrical symmetry of the lamellar interface by calculating the 2D radial distribution functions for the ions located within each pair of shells described above. As an example, Figure 3 describes the average 2D radial distribution function between the pairs of ions both located within the first shell in contact with the charged lamellae in the interlamellar domain. It contains the strongest interionic correlation since the ionic densities are highest at contact with the surface of the colloids^{7,8} (see Figure 2). Furthermore, the long range of the interionic correlations detected for the divalent counterions located in the interlamellar domain is the consequence of the discrete distribution of the charged sites at the surface of the lamellae: the strong localization of the divalent counterions sandwiched between two facing charged sites²³ propagates the interionic correlations to large distances.

The third-order contribution (eq 5d) and further orders are neglected in this calculation.

III. Results and Discussion

Figure 4 displays the variation of the interfacial energy and entropy as a function of the separations between the lamellae neutralized by mono and divalent counterions. In both cases,

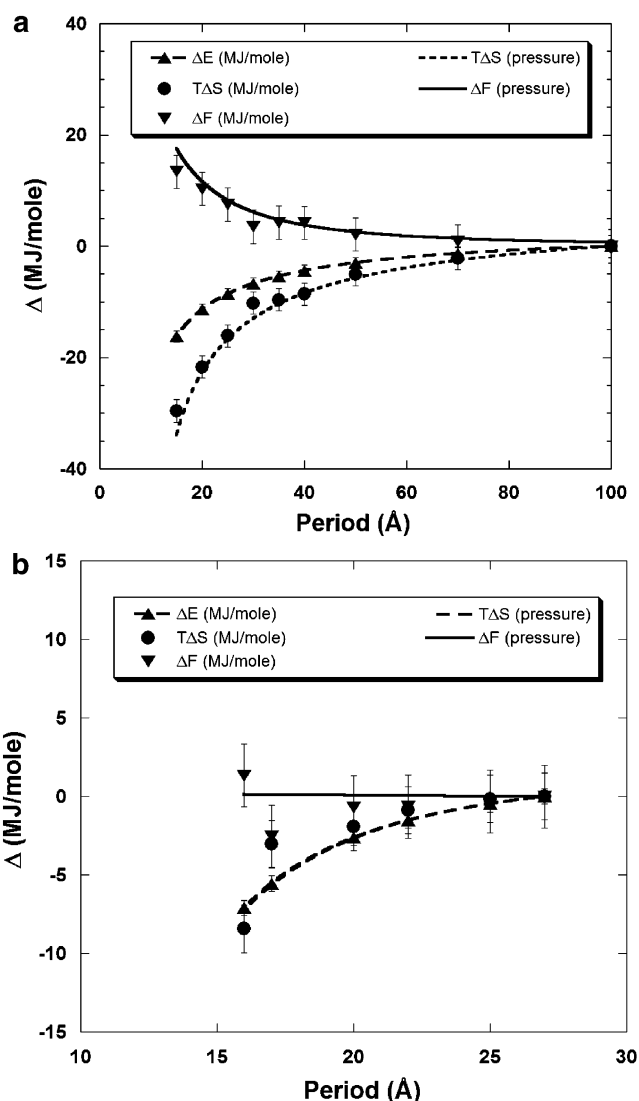


Figure 4. Variation of the interfacial free energy with its energetic and entropic contributions for lamellae neutralized by sodium (a) and calcium (b) cations. The continuous curve results from an analytical integration of the power law fitted on the variation of the swelling pressure (see text).

the net electrostatic energy is attractive because the ion/lamella attractions overcome the ion/ion and lamella/lamella repulsions. The variation of the interfacial entropy calculated for monovalent counterions is more negative than the energy variation, leading to a net repulsion (Figure 4a). The order of magnitude of the free energy difference detected during the swelling of the lamellae appears excessive (15 MJ/mol). However, the free energy is an extensive thermodynamical property, and after division by the total number of charged sites, the free energy variation induced by the swelling (1.2 kJ/mol) becomes commensurable with the thermal energy. This result also illustrates the entropic origin of the net repulsion between charged colloids neutralized by monovalent counterions. By contrast, the entropy variation calculated for divalent counterions nearly superimposes on the energy variation of the interface leading to a flat free energy profile (see Figure 4b).

To check the validity of our direct derivation of the free energy, the net interlamellar pressure is evaluated from the contact and electrostatic forces (see section II, parts B and C). For charged interfaces neutralized by monovalent counterions, the electrostatic contribution is almost negligible (Figure 5a)

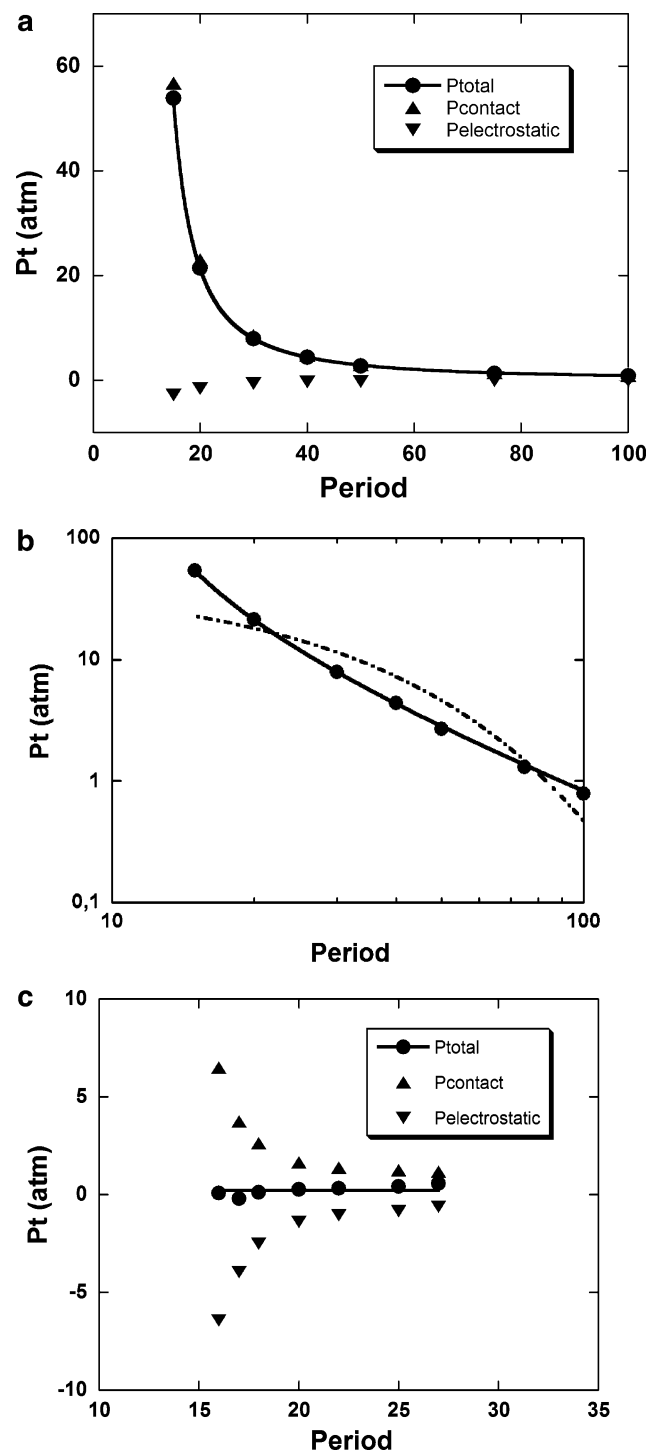


Figure 5. Net interfacial pressure with its contact and electrostatic components calculated for charged lamellae neutralized by sodium (a and b) and calcium (c) cations. A logarithmic scale is used in Figure 4b to better illustrate (see text) the power law variation (continuous line) by contrast with an exponential law (dashed line).

and the pressure is driven by the difference between the contact pressure evaluated in the intralamellar and outer-lamellar domains (see Figure 2).

In the case of charged lamellae neutralized by monovalent counterions, interionic correlations are negligible^{4–9} and the Poisson–Boltzmann equation may be used to predict the interfacial swelling pressure. For a saltfree suspension, an analytical solution is available,^{24–25} leading to a power law variation of the swelling pressure.²⁴ This prediction is confirmed by our Monte Carlo simulations: as shown in Figure 5b, the

pressure is perfectly fitted by a power law

$$\text{pressure} = \frac{1012}{(P - 8.65)^{1.59}} (\text{atm}) \quad (6)$$

where P is the period of the interface (i.e. the interlamellar separation (D) plus the lamella thickness, expressed in Å). The same power law was already reported for charged colloids of any shape (lamellae,²⁴ disks,¹¹ cylinders,¹² spheres^{12,26}). By contrast, in the presence of salt and under the so-called Weak Overlap Approximation (i.e. when $\kappa D > 1$), the swelling pressure evolves according to an exponential law

$$\text{pressure} = \frac{2\sigma^2}{\epsilon_0 \epsilon_r} \exp(-\kappa D) \quad (7a)$$

where D is the interlamellar separation, σ the surface charge density of the lamellae, and κ^{-1} the Debye screening length evaluated on the basis of the salt concentration (c_s):

$$\kappa = \sqrt{\frac{2e^2 c_s}{\epsilon_0 \epsilon_r kT}} \quad (7b)$$

As a consequence and in contrast with recent statements,^{27–28} the counterions neutralizing the electric charges of the polyions cannot contribute to the damping of their repulsion. Added salt is required to detect an exponential damping of the electrostatic repulsion (see Figure 5b) between charged colloids^{24,29} since the Debye screening length is defined only on the basis of the salt concentration of the suspension.^{3,30}

By integrating analytically eq 6, we obtain another power law reproducing the variation of the free energy per charged site

$$\Delta F = \frac{5.29}{(P - 8.65)^{0.59}} (\text{kJ/mole}) \quad (8)$$

which matches perfectly the results displayed in Figure 4a. The perfect matching (see Figure 4a) between the entropy variation deduced from this integration of the equation of state and the entropy directly obtained by using eq 5, parts a–c, is another consequence of our approach. The net force calculated for charged interfaces neutralized by divalent counterions is almost zero because of the cancellation between the weak repulsion induced by the contact force and the electrostatic attraction between the lamellae (see Figure 5c). This result is totally compatible with the flat free energy profile displayed in Figure 4b, further validating our numerical procedure used to reproduce the influence of the interionic correlation in the derivation of the interfacial entropy.

The first- and second-order contributions to the interfacial entropy are also displayed in Figure 6. For monovalent counterions, the second-order contribution is almost negligible and the mixing entropy reproduces more than 95% of the total entropy (see Figure 6a). This result is not surprising since the interionic correlations are negligible for charged interfaces neutralized by monovalent counterions (see Figure 3). In contrast, the second order contribution to the entropy of charged interfaces neutralized by divalent counterions has the same order of magnitude as the mixing entropy (see Figure 6b) and thus cannot be neglected. Furthermore, from this result, one may expect that higher-order contributions can contribute significantly to the free energy of charged interfaces characterized by a stronger electrostatic coupling (i.e., for tri- or tetravalent counterions, for higher surface charge densities or for weaker

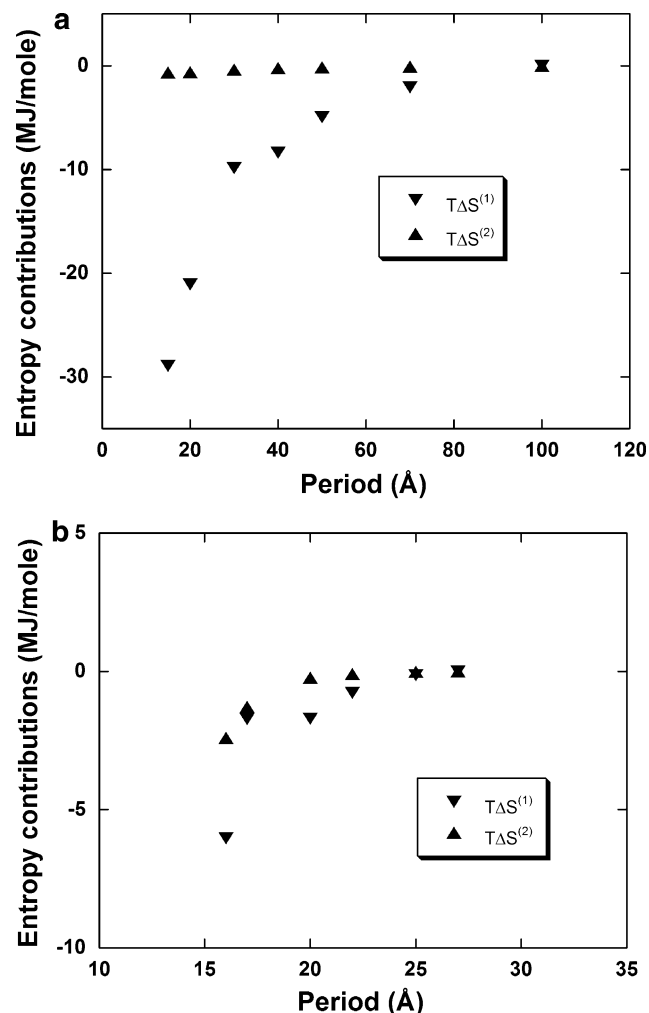


Figure 6. First and second-order contributions to the interfacial entropy calculated for charged lamellae neutralized by sodium (a) and calcium (b) cations.

dielectric constants), because of the simultaneous increase of the influence of the interionic correlations.

Such direct derivation of the free energy of charged interface was already proposed^{11,12} before but it was limited to the evaluation of the first-order contribution (the ideal mixing entropy). As a consequence, that approach was limited to charged colloids with a weak electrostatic coupling (i.e. neutralized by monovalent counterions). This direct entropy derivation, by including second-order contributions, was already successfully applied to describe the thermodynamic behavior of other condensed phases (liquid sodium,³¹ bulk water,³² Lennard-Jones fluids³³). To our knowledge, this approach is used for the first time for the quantification of the stability of charged interfaces.

IV. Conclusions

(N, V, T) Monte Carlo simulations were performed to derive the contribution from the interionic correlations on the stability of charged interfaces neutralized by mono- and divalent counterions. The entropy characterizing the ionic distribution between

two charged lamellae is evaluated on the basis of a multiparticle correlation expansion limited to the second-order contribution. In both cases, quantitative agreement is found with the free energy and the entropy derived from an analytical integration of the variation of the net interlamellar pressure. This study illustrates the large influence of the interionic correlations on the entropy of charged interfaces under strong coupling conditions, i.e., neutralized by divalent counterions.

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