Binding of Similarly Charged Plates: A Global Analysis

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Similarly and highly charged plates in the presence of multivalent counter ions attract each other, leading to electrostatically bound states. Using Monte-Carlo simulations we obtain the inter-plate pressure in the global parameter space. The equilibrium plate separation, where the pressure changes from attractive to repulsive, exhibits a novel unbinding transition. A systematic and asymptotically exact strong-coupling field-theory yields the bound state from a competition between counter-ion entropy and electrostatic attraction, in agreement with simple scaling arguments.

Experimentally, it has been known for a long time that highly charged planar surfaces attract each other in the presence of multivalent counter ions, inducing bound states. This electrostatic binding restricts the swelling of calcium clay particles and leads to much reduced water uptake of charged lamellar membrane systems. Attractive forces between charged surfaces have also been observed with the surface force apparatus. Monte-Carlo simulations indeed confirmed that for a given surface charge density there exists a threshold counter-ion valence above which attraction can be observed over some range of plate separations.

Theoretically, these observations came as a surprise, since the mean-field or Poisson-Boltzmann (PB) theory, which works usually quite well for charged systems, predicts only repulsive forces between charged objects. This contradiction between observation and PB prediction resulted in an immense theoretical activity, which aimed at understanding the simple model of two uniformly and similarly charged planar surfaces interacting across a gap of width $d$ filled with point-like counter ions. Clearly, reality is much more complicated due to additional interactions, but even this simple model, which we will consider in the following, is quite challenging. A number of approaches were proposed which incorporate counter-ion correlations that are neglected within PB. The first were integral-equation theories, perturbative expansions around the PB theory, and local density-functional theory, which compare well with simulation results and exhibit attraction. If the two plates are far apart from each other, the counter-ion clouds can be viewed as condensed on the plates, and the resulting simplified model can be solved within a Gaussian or harmonic-plasmon approximation. These approaches either involve numerics and do not provide much physical insight, or they are valid for large separations and cannot be used to characterize the bound state.

Of great significance is the fact that when the electrostatic force is attractive, the equilibrium distance $d^*$ between the plates is smaller than the typical lateral distance $a$ between counter ions (as we will demonstrate later on), thus rendering a quasi-two-dimensional layer of counter ions. In the first part of this paper, we will use this fact and present a scaling argument for the attraction between two plates, valid for $d \ll a$. We will then demonstrate that this scaling analysis is equivalent to the leading order of a systematic field-theory, valid in the strong-coupling (SC) limit (corresponding to large plate-charge density $\sigma$ or large counter-ion valence $q$), where it agrees with extensive Monte-Carlo (MC) simulations. Our MC results span the complete parameter space. Whenever attractive forces between the plates exist, they induce a bound equilibrium state, which exhibits a novel unbinding transition.

The simple scaling argument for attraction between charged plates starts with partitioning the system into isolated counterions sandwiched between two finite plate segments of area $A = q/2\sigma$. Neglecting ion-ion interactions should be valid for $d \ll \sqrt{A}$. Denoting the distance between the counterion and the plates as $x$ and $d - x$, respectively, we obtain for the electrostatic interaction energies, in units of $k_BT$ and for $d \ll \sqrt{A}$, the results $W_1 = 2\pi \ell_B q \sigma x$ and $W_2 = 2\pi \ell_B q \sigma (d - x)$, respectively, as follows from the potential at an infinite charged wall and omitting constant terms. The sum of the two interactions is $W_{1+2} = W_1 + W_2 = 2\pi \ell_B q \sigma q d$ which shows that i) no pressure is acting on the counterion since the forces exerted by the two plates exactly cancel and ii) that the counterion mediates an effective attraction between the two plates. The interaction between the two plates is proportional to the total charge on one plate, $A\sigma$, and for $d \ll \sqrt{A}$ given by $W_{12} = -2\pi \ell_B A \sigma^2 d$. Since the system is electroneutral, $q = 2A\sigma$, the total energy is $W = W_{12} + W_1 + W_2 = 2\pi A \ell_B \sigma^2 d$, leading to an electrostatic pressure $P_e = -\partial (W/A)/\partial d = -2\pi \ell_B \sigma^2$. The two plates attract each other. The entropic pressure due to counter-ion confinement is $P_{en} = 1/Ad = 2\sigma/qd$. The equilibrium plate separation is characterized by zero total pressure, $P_{tot} = P_e + P_{en} = 0$, leading to an equilibrium plate separation $d^* = 1/\pi \ell_B q \sigma$. By construction, the derivation for $d^*$ is valid only for $d^* < a$.
(where $a$ is the average lateral distance between ions as defined by $\pi a^2 = q / 2\sigma$), equivalent to the condition $\Xi = 2\pi^2 \ell_B^2 \sigma^3 > 4$, i.e., for large values of the coupling constant $\Xi$. Surprisingly, these results for $P_{\text{tot}}$ and $d^*$ become exact in the SC limit $\Xi \to \infty$, as we will demonstrate in the following. In fact, the attraction between charged plates, as derived here for $d \ll a$, is conceptually simpler than the PB result of repulsion, because the latter case involves many-body effects.

To proceed with our systematic field theory, consider

$$\mathcal{H} = \frac{\ell_B}{2} \int d\mathbf{r}[q \hat{\rho}(\mathbf{r}) - \sigma \delta(z) - \sigma \delta(d-z)]v(\mathbf{r} - \mathbf{r}')[q \hat{\rho}(\mathbf{r}') - \sigma \delta(z') - \sigma \delta(d-z')] - \int d\mathbf{r} \hat{\rho}(\mathbf{r}) h(\mathbf{r})$$

(2)

where $v(\mathbf{r}) = 1/r$ is the Coulomb interaction and the field $h$ has been added to calculate density distributions later on. The characteristic length scales are the Bjerrum length $\ell_B = e^2 / 4\pi \varepsilon \kappa_B T$ and the Gouy-Chapman length $\mu = 1 / 2\pi \ell_B q \sigma$, which measure the distance at which the interaction between two unit charges and between a counter ion and a charged wall reach thermal energy, respectively. Rescaling all lengths by the Gouy-Chapman length according to $\mathbf{r} = \mu \tilde{\mathbf{r}}$ and $d = \mu \tilde{d}$, the Hamiltonian becomes

$$\mathcal{H} = \frac{1}{8\pi^2 \Xi} \int d\tilde{\mathbf{r}}' [2\pi \Xi \tilde{\rho}(\tilde{\mathbf{r}}') - \delta(\tilde{z}) - \delta(\tilde{d} - \tilde{z})]v(\tilde{\mathbf{r}} - \tilde{\mathbf{r}}') [2\pi \Xi \tilde{\rho}(\tilde{\mathbf{r}}') - \delta(\tilde{z}') - \delta(\tilde{d} - \tilde{z}')] - \int d\tilde{\mathbf{r}}' \tilde{\rho}(\tilde{\mathbf{r}}) h(\tilde{\mathbf{r}})$$

(3)

and thus only depends on the coupling parameter $\Xi = 2\pi q^2 \ell_B^2 \sigma$. At this point we employ a Hubbard-Stratonovitch transformation, similar to previous implementations of a field theory for charged systems [13], followed by a Legendre transformation to the grand-canonical ensemble, $Q = \sum_{\mathbf{r}} \lambda^N Z_{\mathbf{r}}$, introducing the fugacity $\lambda$. The inverse Coulomb operator follows from Poisson’s law as $v^{-1}(\mathbf{r}) = -\nabla^2 \delta(\mathbf{r}) / 4\pi$, which leads to

$$Q = \int \frac{D\phi}{Z_v} \exp \left\{ -\frac{1}{8\pi \Xi} \int d\mathbf{r} \left[ (\nabla \phi(\mathbf{r}))^2 - 4\mu \delta(\tilde{z}) \phi(\mathbf{r}) - 4\mu \delta(\tilde{d} - \tilde{z}) \phi(\mathbf{r}) - 4\lambda \theta(\tilde{z}) \theta(\tilde{d} - \tilde{z}) e^{\lambda(\mathbf{r}) - \phi(\mathbf{r})} \right] \right\}$$

(4)

where we introduced the notation $Z_v = \sqrt{\det v}$ and the rescaled fugacity $\lambda$ is defined by $\lambda = 2\pi \lambda \mu^2 \Xi = \lambda(2\pi s^2 \ell_B)$. The expectation value of the counter-ion density, $\tilde{\rho}(\mathbf{r})$, follows by taking a functional derivative with respect to the generating field $h$, $\rho(\mathbf{r}) = \delta \ln Q / \delta h(\mathbf{r}) \mu^3$, giving rise to

$$\tilde{\rho}(\mathbf{r}) = \frac{\rho(\mathbf{r})}{2\pi \ell_B \sigma^2} = \Lambda(\exp(-\tilde{\phi}(\mathbf{r}))).$$

(5)

The normalization condition for the counter-ion distribution, $\mu \int d\tilde{z} \tilde{\rho}(\tilde{z}) = 2\sigma / q$, which follows directly from the definition of the grand-canonical partition function, leads to

$$\Lambda \int_0^{\tilde{d}} d\tilde{z} \exp(-\tilde{\phi}(\tilde{z})) = 2.$$  (6)

This is an important equation since it shows that the expectation value of the fugacity term in Eq.(5) is bounded and of the order of unity. Let us first repeat the saddle-point analysis, which, because of the structure of the action in Eq.(5), should be valid for $\Xi \ll 1$. The saddle-point equation reads $\partial^2 \tilde{\phi}(\tilde{z}) / \partial \tilde{z}^2 = 2\Lambda e^{-\tilde{\phi}(\tilde{z})}$. The solution of this differential equation is $\tilde{\phi}(\tilde{z}) = 2\ln \cos \left( \Lambda^{1/2}[\tilde{z} - \tilde{d}/2] \right)$. The normalization condition leads to the equation $\Lambda^{1/2} \tan[d \Lambda^{1/2}/2] = 1$, which is solved by $\Lambda \simeq 2 / d$ for $d \ll 1$ and $\Lambda \simeq \pi^2 / 4d^2$ for $d \gg 1$. From Eq.(6), the rescaled density distribution of counter ions is given by the well-known PB result

$$\tilde{\rho}(\tilde{z}) = 1 / \cos^2 \left( \Lambda^{1/2}[\tilde{z} - \tilde{d}/2] \right).$$

(7)

Let us now consider the opposite limit, when the coupling constant $\Xi$ is large. In this case, the saddle-point approximation breaks down, since the prefactor in front of the action in Eq.(6) becomes small. Since the fugacity term is bounded, as evidenced by Eq.(5), one can expand the partition function (and also all expectation values) in powers of $\Lambda / \Xi$ (which is equivalent to a virial expansion). For the expectation value determining the density Eq.(6) the leading two orders in the virial expansion are

$$\langle e^{-\phi(\mathbf{r})} \rangle = e^{-\Xi\langle v(\mathbf{r}) \rangle / 2} + \frac{\Lambda e^{-\Xi\langle v(\mathbf{r}) \rangle}}{2\pi \Xi} \int d\mathbf{r} \left( e^{-\Xi\langle v(\mathbf{r}) \rangle} - 1 \right).$$

The normalization condition Eq.(6) can then be solved by an expansion of the fugacity in inverse powers of the coupling constant, $\Lambda = \Lambda_0 + \Lambda_1 / \Xi + \ldots$. We obtain $\Lambda_0 = 2e^{\Xi\langle v(\mathbf{r}) \rangle} / d$ and thus the density distribution is (in agreement with our scaling analysis) to leading order indeed a constant given by
In Fig. 1a we show counter-ion density profiles obtained using MC simulations [14] for small coupling parameter $\Xi = 0.5$ for various plate distances, which are well described by the PB profiles Eq. (6) shown as solid lines. As suggested by our scaling analysis, the asymptotic SC result Eq. (8) should be valid for $d/a = d/\Xi^{1/2} < 1$ only, since otherwise ion-ion interactions become important. For $d = 3/2$ (open diamonds) we find $d/a = 0.15$, and indeed Eq. (8) is accurate. For $d = 10$ (open stars) we find $d/a = 1$, the density profile is neither described by Eq. (8) nor (9). Finally, for $d = 30$ (open stars) we find $d/a = 3$, the two layers are decoupled and the density profile is described by a double exponential $\rho(\tilde{z}) = (e^{-\tilde{z}} + e^{-\tilde{z}-d})/(1-e^{-d})$ (dashed-dotted line), which is the superposition of the density profiles of two isolated charged surfaces in the SC limit (1). The crossover from PB to SC is demonstrated in Fig. 2, where we plot density profiles for fixed plate separation $\tilde{d} = 2$ for various coupling parameters $\Xi$.

The first term is the entropic pressure due to counterion confinement, the second term is due to electrostatic interactions between the counterions and the charged plates. Numerically, the contact ion density $\tilde{\rho}(\tilde{d})$ is obtained from the density profiles by extrapolation. In Fig. 3 we show numerical pressure data for various values of $\Xi$. Attraction (negative pressure) is obtained for $\Xi > 10$. The numerical pressure for $\Xi = 0.5$ (open diamonds) agrees well with the PB prediction (solid line), which from Eqs. (9) and (10) is given by $P = \tilde{d}^2/12 - 2$. Incidentally, this is exactly the scaling prediction for the pressure derived in the beginning of this paper.
Finally, combining all pressure data, we obtain the global phase diagram shown in Fig. 4, featuring two regions where the inter-plate pressure is attractive and repulsive. The dividing line between those regions, which corresponds to the equilibrium plate separation \( \tilde{d}^* \) in the bound state, is determined over 4 decades of the coupling constant \( \Xi \). In the limit of large coupling constants, the phase boundary saturates at \( \tilde{d}^* = 2 \), in agreement with our scaling argument and the leading result of our SC theory. The threshold coupling constant to observe attraction between charged plates is \( \Xi^* \approx 10 \). As \( \Xi \to \Xi^* \) from above, the equilibrium plate separation diverges continuously to infinity. This constitutes a novel unbinding transition, which experimentally could be observed with charged lamellar or clay systems by raising the temperature.

The plate separation equals the lateral ion-distance on a line in Fig. 4 determined by \( d/a = \tilde{d}/\Xi^{1/2} = 1 \), which crosses the equilibrium-separation line at \( \tilde{d} \approx 3 \). For the most part of the equilibrium-separation line in Fig. 4 the counter-ion distribution is therefore indeed two-dimensional, and many-ion effects can be neglected except very close to \( \Xi^* \). Correlations between counter ions, except the lateral exclusion correlation which keeps ions apart, are therefore mostly unimportant in the bound state. This explains why the simple single-ion scaling argument advanced in the beginning, which turns out to be exact in the limit \( \Xi \to \infty \), works so well. More detailed comparison between MC and next-leading terms of our SC theory, which are equivalent to higher-order virial terms, together with a detailed discussion of the significance of Wigner crystallization (which occurs at \( \Xi \approx 15600 \) in the limit \( \tilde{d} \to 0 \)) will be published shortly.

FIG. 3. MC results for the rescaled pressure \( \tilde{P} = P/2\pi\ell_B\sigma^2 \) as a function of the rescaled plate separation \( \tilde{d} = d/\mu \) for the same parameter values as in Fig. 2 (and \( \Xi = 20 \), open squares), compared with the PB prediction \( \tilde{P} = \Lambda \) (solid line) and the SC prediction \( \tilde{P} = 2/\tilde{d} - 1 \) (broken line).

FIG. 4. Global phase diagram featuring the regions of repulsive and attractive pressure as a function of the rescaled plate separation \( \tilde{d} = d/\mu \) and coupling strength \( \Xi \). The dividing line denotes the equilibrium plate separation \( \tilde{d}^* \), which saturates at \( \tilde{d}^* = 2 \) for \( \Xi \to \infty \) and which diverges as \( \Xi \) approaches the critical value \( \Xi^* \approx 10 \) from above.

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