Quasi-universality in mixed salt-free counterion systems

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Abstract – The screening of plate-plate interactions by counterions is an age-old problem. We revisit this classic question when counterions exhibit a distribution of charges. While it is expected that the long-distance regime of interactions is universal, the behaviour of the inter-plate pressure at smaller distances should *a priori* depend rather severely on the nature of the ionic mixture screening the plate charges. We show that this is not the case, and that for comparable Coulombic couplings, different systems exhibit a quasi-universal equation of state.

Introduction. – Colloidal suspensions are made up of macromolecules in a more or less polar solvent. The presence of charged groups at the surface of the macromolecules may lead to repulsive interactions, providing a mechanism to counteract ubiquitous van der Waals attractions, that would otherwise lead to aggregation, and an instability of the suspension [1]. It is however possible to minimize and sometime cancel these van der Waals forces, *e.g.*, by refractive index matching [2]. Integrating over microscopic degrees of freedom (solvent, microions), one obtains the free energy for any given fixed configuration of macromolecules, from which the equilibrium force felt by each macroion derives [3,4]. The resulting so-called effective potential is the object of central interest in the present paper. We focus on the simplest possible setting where two charged planar macromolecules confine the solvent and charge-compensating counterions in a slab in an otherwise salt-free environment. More specifically, we are interested in the effect of counterion polydispersity, in the sense that they may bear different charges. Understanding such setups has importance for systems such as, *e.g.*, mixed Na/Ca-bentonite clay systems [5] or lamellar surfactant systems with mixed counterions [6]. A central result reported is that of a certain universality of the effective plate-plate potential. To illustrate the statement, we will consider rather extreme counterion charge distribution $n(q)$: while counterions naturally bear a multiple of the elementary charge ($q = 1$ for monovalent ions, $q = 2$ for divalent ions, etc.), and, therefore, have a $n(q)$ with

discrete support, we will address cases in which $n(q)$ is continuous, to maximize the effect of non-monodispersity.

It is known that the effective plate-plate potential (or equivalently in the present case, the pressure), turns from all-distance repulsive under small Coulombic couplings, to a more complex dependence under larger coupling, with repulsion at small distances, attraction in some intermediate range, and repulsion again at large distances. When all ions have the same elementary charge $-e$, quantification of coupling is operated by a dimensionless parameter Ξ, which is a measure of inverse temperature β or, equivalently, of the plate surface charge σe. In a solvent of permittivity ϵ, we have $\Xi \propto \sigma \ell_B^2$, where $\ell_B = \beta e^2/\epsilon$ is the Bjerrum length. This dimensionless quantity measures the relative strengths of the ion-ion to ion-surface interactions and tells us how well the ions can correlate with each other (and tells us how far from a mean-field description we are). As a rule of thumb, the mean field holds for $\Xi < 1$ [7] and the Wigner crystallization occurs at $\Xi > 10^4$ [8]. Whereas the prototypical problem with a unique type of counterions (referred to as the monodisperse case with $q = 1$) is well documented [7,9–11], we present here a combination of analytical and numerical results for polydisperse systems. Counterions have charge $-qe$ with a density distribution $n(q)$. We seek several types of universal features: a) within a given family of polydisperse distribution $n(q)$, a rather down-to-earth type amounts to finding the proper set of reduced variables, making, if possible, the reduced pressure independent of the polydispersity;

b) we are interested in changing the type of polydispersity, considering distinct families of functions $n(q)$. Given the qualitatively distinct behavior at small and large couplings, it is certainly essential here to keep track of this coupling in the description.

Yet, it should be clear from the outset that there is another and broader level of universality in the large-distance (d) behavior of the pressure. Indeed, irrespectively of the coupling parameter, the two plates interact weakly at large d. There, one can expect counterions to effectively "dress" the plates, modifying their effective charge (that it is not necessary to define in a more rigorous manner), with in between the plates, a weak density of ions remaining, only those with smallest valence q_{min}. Thus, we expect the physics of interactions to fall at large d in the mean-field category, which has the remarkable property to be independent of the macroion charge [12]. This is a consequence of the $(\ell_B d^2)^{-1}$ dependence of pressure, which does not leave room for any dependence on σ, for dimensional reasons. We expect this result to be valid as long as one can define a Bjerrum length ($q_{min}^2 \ell_B$) associated to the population of smallest valence, which means as long as $q_{min} > 0$ (see foonote [1]).

As alluded to, we consider a system of two plates at distance d, both having uniform surface charge σe, and neutralized by counterions in the slab $-d/2 \leq x \leq d/2$. Denoting the maximum valence by q_{max}, electroneutrality requires that

$$\int_{q_{min}}^{q_{max}} n(q) \, q \, dq = 2\sigma, \tag{1}$$

where $n(q)$ is the total (surface) density of ions having valence q.

Monte Carlo simulations. – We have performed Monte Carlo simulations in a quasi-2D geometry in the canonical ensemble of a salt-free system. Long-ranged electrostatic interactions are handled with Ewald summation techniques corrected for quasi–2-dimensionality by introducing a vacuum slab in the z-direction perpendicular to the surfaces [13,14]. We verified that our vacuum slab is sufficiently wide not to influence the results. All simulations consisted of 512 point charges while the surfaces are modeled as structureless uniformly charged infinite plates, in agreement with the following analytical treatment, which addresses some limiting cases. Simulations were performed both for equimolar binary mixtures with charge ratios 2:1, 3:1, and 10:1 (the first two due to their relevance for realistic ionic systems, and the last one to probe the system in an extreme situation[2]) as well as for a continuous flat distribution of charges, $q \in [0, q_{max}]$ (and thus $\langle q \rangle = q_{max}/2$). Figure 1 shows the pressure curves

Table 1: Comparison between the different moments of the valence for the studied counterion mixtures.

Counterion mixture	$\langle 1/q \rangle \langle q \rangle$	$\langle q^2 \rangle / \langle q \rangle^2$	$\langle q^3 \rangle / \langle q \rangle^3$
Mono	1	1	1
Mix 50/50 2:1	9/8	10/9	4/3
Mix 50/50 3:1	4/3	5/4	7/4
Mix 50/50 10:1	$\simeq 3.03$	$\simeq 1.67$	$\simeq 3.01$
Flat	∞	4/3	2

$\widetilde{P} \equiv \beta P / (2\pi \ell_B \sigma^2)$ as a function of the reduced plate-plate separation $\tilde{d} \equiv d/\mu$, with μ defined as the inverse ion averaged Gouy-Chapman length $\mu = [2\pi \ell_B \sigma \langle q \rangle]^{-1}$ and $\langle q \rangle$ is the mean charge of the ions. Density profiles $\tilde{\rho} \equiv \rho / (2\pi \ell_B \sigma^2)$ are also shown at $\tilde{d} \simeq 7.9$ for three different coupling parameters $\Xi = 2\pi \langle q \rangle^3 \ell_B^2 \sigma$. The pressure curves reasonably collapse onto each other at small plate-plate separations. This feature is however not an exact property, and for this reason, it is referred to as "quasi-universal"[3]. For the larger coupling parameters ($\Xi = 17.5$ and 158) one sees the well-documented although counterintuitive like-charge attraction, driven by ion-ion correlations. Impressively enough, even the attractive minima do coincide fairly well, both in magnitude and width, for the same coupling parameter, irrespectively of the mixture type. We want to stress that there exist other ways to define coupling parameters (*e.g.*, $\Xi \sim \langle q^3 \rangle$ rather than $\Xi \sim \langle q \rangle^3$) in mixed systems, but only by using $\langle q \rangle^3$ do we find a good enough collapse. A table of moments corresponding to the various cases investigated in the present work, and also useful for the analytical treatment, is given in table 1. At $\Xi = 17.5$, one does however observe small discrepancies, even at small separations, between the different mixtures of ions. These small discrepancies are more pronounced at intermediate and long separations, where the (modest) repulsive barrier seems to be stronger (more repulsive) as the charge ratio of the binary mixture increases; the "flat" charge distribution case appears intermediate between the binary systems with charge ratios 3:1 and 10:1. The violations to quasi-universality appear maximal on the 10:1 case, but even there, the location of the attractive minimum is well predicted by the proposed rescaling. Also, the other coupling parameters (1.58 and 158) exhibit minor discrepancies from intermediate to larger separations, but the variation induced by ionic composition is small compared to the absolute values (note the different pressure scales in the figures). Note further that density profiles themselves do exhibit a similar "quasi-universal" property. With the present model, it is known that the inter-plate pressure is directly related to ionic density at contact with the plates (this is the contact theorem, used below). Thus,

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[1]When $q_{min} \to 0$, we thus get a diverging pressure, which is indicative of the fact that the pressure, in those cases, ceases to exhibit a power in distance with exponent -2, but can be longer-ranged.

[2]A situation in which the relevance of the mean-field picture would be somewhat questionable.

[3]A simple means to see that full universality cannot hold is to restrict to those polydisperse situations having $q_{min} > 0$, for which the asymptotic large-distance pressure can be advocated to scale like $(q_{min} d)^{-2}$.
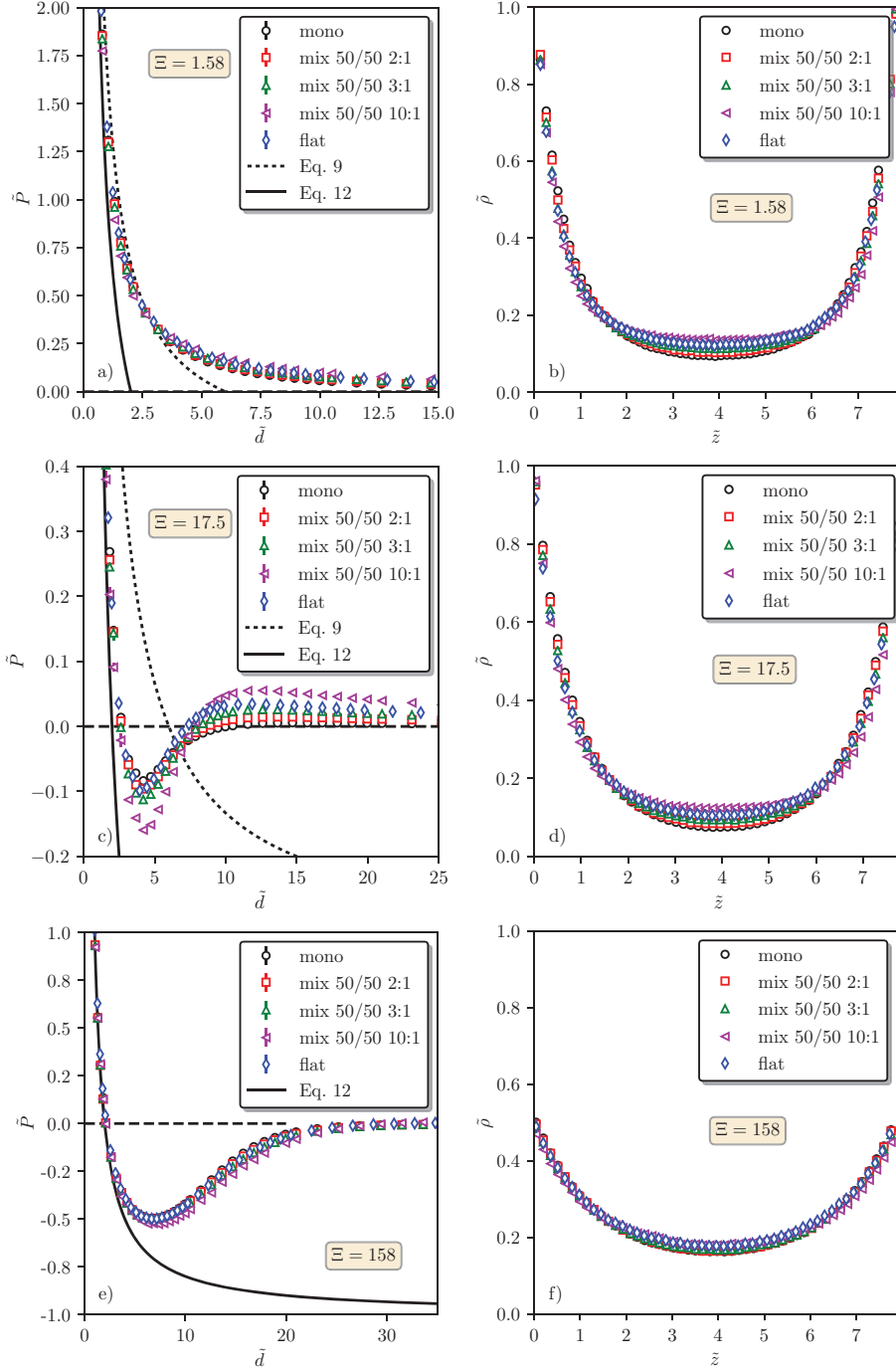
Fig. 1: (Colour online) (a), (c), (e): normalized pressure *vs.* normalized separation for three different coupling parameters $\Xi = 1.58, 17.5$ and 158. Symbols: Monte Carlo results; lines: analytic expressions. (b), (d), (f): density profiles between the two charged surfaces (data obtained from Monte Carlo simulations) at $\tilde{d} \simeq 7.9$ at the three coupling parameters.

two systems showing similar pressures should also have similar contact densities. Yet, nothing guarantees that the whole profiles will collapse. In particular, one can scrutinize mid-plate features, that allow for another (equivalent) calculation of the pressure, that can be decomposed into three terms in the primitive model: $\tilde{P}_{\text{conc}}$, $\tilde{P}_{\text{corr}}$, and $\tilde{P}_{\text{hc}}$. The first stems from the mid-plane concentration (momentum flux over the mid-plane), the second is an energetic

correlation pressure (and absent in mean-field treatments) and the third is a collisional hard-core term (here strictly zero as we do not use any hard-core radii). The fact that mid-plane concentrations and the pressures are the same irrespectively of the mixture as soon as the reduced variables are the same ($\tilde{d}$ and Ξ) shows us that the value of the correlation term is the same irrespectively of the mixture. Overall, the results show a decent agreement, and

the proposed reduced parameter set (*i.e.*, Ξ, $\tilde{P}$, and $\tilde{d}$) captures well the dominant quasi-universal behavior.

Analytic treatment. – We start by weakly coupled systems, where the Poisson-Boltzmann mean-field treatment should hold [4,7]. Introducing the dimensionless electrostatic potential ϕ, one has to solve

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = 4\pi\ell_B \int_{q_{\min}}^{q_{\max}} f(q)qe^{q\phi(x)}\,\mathrm{d}q \qquad (2)$$

which appears in the form of an implicit formulation. Indeed, the volume density of species q can be written $f(q)\exp(q\phi)$, and the normalization function $f(q)$ is *a priori* unknown. It relates to the chosen $n(q)$ through

$$n(q) = \int_{-d/2}^{d/2} f(q)\,e^{q\phi(x)}\,\mathrm{d}x. \qquad (3)$$

Therefore, starting from $n(q)$, $f(q)$ is not known before eq. (2) has been solved, this equation itself requiring the knowledge of $f(q)$. Since the large-d asymptotics is constrained by the argument presented above, we focus on short-d features. It is for that purpose useful to choose $\phi(0) = 0$, where the symmetry and Gauss theorem further impose $\phi'(0) = 0$ and $\phi'(d/2) = 4\pi\ell_B\,\sigma$. Taylor-expanding ϕ, which is even, we have

$$\phi(x) \sim a_1 x^2 + a_2 x^4 + \ldots \qquad (4)$$

$$\text{with } a_1 = 2\pi\ell_B \int q\,f(q)\,\mathrm{d}q \qquad (5)$$

$$a_2 = \frac{2}{3}\,(\pi\ell_B)^2 \left[\int q\,f(q)\mathrm{d}q\right]\left[\int q^2\,f(q)\,\mathrm{d}q\right], \qquad (6)$$

where the last two lines are obtained by inserting the expansion into eq. (2). Restricting to the quadratic term gives the dominant contribution to the pressure, that reads

$$\beta P = \int f(q)\,\mathrm{d}q, \qquad (7)$$

meaning that within the present mean-field description, it is given by the mid-plane ionic density, a classic result stemming from the fact that the electric field vanishes at this point. Making use of eq. (3) allows us to write

$$\beta P = \frac{1}{d}\int n(q)\mathrm{d}q - \frac{\pi\ell_B}{6}\left[\int q n(q)\mathrm{d}q\right]^2. \qquad (8)$$

Remembering electroneutrality, and defining a (Gouy-Chapman) length as above $\mu = [2\pi\ell_B\sigma\langle q\rangle]^{-1}$, where $\langle q\rangle$ is the mean valence of the distribution[4], we introduce the reduced separation $\tilde{d} = d/\mu$ and obtain

$$\tilde{P} \equiv \frac{\beta P}{2\pi\ell_B\sigma^2} = \frac{2}{\tilde{d}} - \frac{1}{3}, \qquad (9)$$

which appears in a polydispersity independent form. Note that the term in $2/\tilde{d}$ is nothing but the ideal-gas entropy,

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[4]Note that $\langle q\rangle = \int q\,n(q)\mathrm{d}q / \int n(q)\mathrm{d}q = 2\sigma / \int n(q)\mathrm{d}q$.

necessarily dominant at very small separations where the entropy of confinement overwhelms other contributions to the equation of state. This suggests to use μ defined from $\langle q\rangle$ as the relevant length and consider $\tilde{P}$, as was done for our numerical results. Comparing the expression with the Monte Carlo results, see fig. 1(a), we see that this approximation seems to be valid up to $\tilde{d} \lesssim 3$. It is also instructive to push the expansion one order higher in distance. After some algebra, this yields

$$\tilde{P} = \frac{2}{\tilde{d}} - \frac{1}{3} + \frac{2}{45}\frac{\langle q^2\rangle}{\langle q^3\rangle}\tilde{d}, \qquad (10)$$

where it is seen that the linear contribution in $\tilde{d}$ is $n(q)$-dependent, and in this sense non-universal. Thus, even within the mean field, we should not expect full universality. However, we have shown above by simulations that for practical purposes, the equation of state $\tilde{P}(\tilde{d})$ is remarkably insensitive to the details of the polydispersity function $n(q)$.

Before presenting our conclusion, we show that the same rescaling as in (9) leads to a universal small-distance behavior under strong coupling (*i.e.*, beyond mean field). There, the discrete nature of counterions is essential and every such ion appears far from its neighbors, in the sense that the corresponding distance is larger than the slab width d [15]. As a consequence, the problem is reducible to a single-particle picture, where all species adopt a flat (x-independent) profile with density $n(q)/d$, given that the plates create a vanishing electric field in the slab $-d/2 \leq x \leq d/2$. The contact theorem [16–18] then immediately leads to the pressure, in the form

$$\beta P = -2\pi\ell_B\sigma^2 + \frac{1}{d}\int n(q)\,\mathrm{d}q, \qquad (11)$$

so that we have

$$\tilde{P} = \frac{2}{\tilde{d}} - 1. \qquad (12)$$

The proximity with eq. (9), with the same dominant order, simply stems from the ideal-gas dominant entropy cost of confinement[5]. This result shows that also from the viewpoint of the strong coupling the proposed reduced units $\tilde{d}$ and $\tilde{P}$ are indeed reasonable choices, hence suggesting that also intermediate coupling parameters should be rescaled equivalently. However, unlike eq. (12), eq. (9) is unable to predict like-charge attraction (*i.e.*, $P < 0$). Indeed, such a phenomenon would occur for $\tilde{d} > 6$ from (9), a distance range where our expansion no longer holds. The bottom line is that the mean-field pressure is always repulsive [19–21]. On the other hand, eq. (12) indicates attraction for $\tilde{d} > 2$, which is validated by numerical simulations. Thus, all the above results, numerics and analytics, indicate that the dimensionless quantities $\tilde{d}$ and $\tilde{P}$ are useful

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[5]Under strong coupling, computing the next-order contribution in distance is a difficult task, which requires knowledge of (at least) the local structure of the counterion system [11].

rescalings also for mixed counterion systems. It would be interesting to perform the strong-coupling expansion one order higher, but such a task is beyond the scope of the present paper.

Conclusion. – We have shown that the short-distance effective interactions between two equally charged surfaces exhibit a robust quasi-universal equation of state, irrespectively of the type of mixture of counterions. This requires to introduce suitably defined reduced variables, where the inter-plate distance is measured in units of length, the inverse of which can be viewed as the mean inverse Gouy-Chapman length ($1/\mu = 2\pi\ell_B\,\sigma\langle q\rangle$), where the average is taken over the counterion distribution $n(q)$. In addition, it is of course essential to keep track of Coulombic coupling. While there is no clear-cut definition of a coupling parameter in the present polydisperse situation, we have shown that the parameter $\Xi = 2\pi\langle q\rangle^3\ell_B^2\sigma$ allows for suitable rescaling. We furthermore see that the collapse extends at separations beyond the validity of our analytic expansion results. Deviations, from the mono-disperse case, at short separations are, however, seen to grow as the charge moments are increased (*i.e.*, the polydispersity) and if one is "close" enough to the onset of attraction, roughly at $\Xi \simeq 5$. However, for realistic mixtures (*i.e.*, charge ratios of 2:1 and 3:1) the collapse works remarkably well. Our approach holds for a salt-free system (counterions only) without any possibility of ion exchange. In an open system (*e.g.*, in contact with a salt reservoir), the mixture composition would vary as a function of the plate separation. At short separations, co-ions would be expelled from the slab, to be released in the reservoir, and one would be left with a salt-free system favoring the high-valence counterions. A complication for such a system is that the distribution might change as a function of separation and hence $\langle q\rangle$. This would result in a change in both μ and Ξ, whereby continuously or discontinuously (*e.g.*, in the case of a phase separation [22]) having a crossover between the different pressure curves. To produce such a curve one would hence need to know how such a distribution varies as a function of separation. In that limiting distance regime, our approach would be applicable accounting for the changed composition of the counterions.

Finally, we note that our results can be viewed as an (approximate) law of corresponding states, where the mean counterion valence $\langle q\rangle$ plays a privileged role over a range of relevant coupling parameters. On the other hand, in the Deby-Hückel treatment of electrolytic systems (where thus microscopic ions of both signs are present), the key quantity is the Debye length, which involves a different moment, $\langle q^2\rangle$. As a first approximation, one could include the salt in our treatment, in a dressed multivalent ion formulation [23][6]. This is left as an open question.

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[6]It is also questionable if the charge symmetry in a $+2/+1$ mixture exhibits high enough charge asymmetry for the dressed multivalent ion theory to be applicable, and this approach would presumably fail for the flat distribution.