Surface Pressure of Charged Colloids at the Air/Water Interface

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Charged colloidal monolayers at the interface between water and air (or oil) are used in a large number of physical and biological applications. Although considerable experimental and theoretical effort has been devoted to the past few decades to investigate such monolayers, their fundamental properties are not yet fully understood. In this paper, we model charged colloidal monolayers as a continuum layer of finite thickness, with separate charge distribution on the water and air sides. The electrostatic surface free-energy and surface pressure are calculated via the charging method and within the Debye-Hückel approximation. We obtain the dependence of surface pressure on several system parameters: the monolayer thickness, its dielectric permittivity, and the ionic strength of the aqueous subphase. The surface pressure scaling with the area, $A$, is found to be $A^{-2}$ in the close-packing limit, and $A^{-3/2}$ in the loose-packing limit. In general, it is found that the surface-pressure is strongly influenced by charges on the air-side of the colloids. However, when the larger charge resides on the water-side, a more subtle dependence on salt concentration emerges. This corrects a common assumption that the charges on the water-side can always be neglected due to screening. Finally, using a single fit parameter, our theory is found to fit well the experimental data for strong to intermediate strength electrolytes.

I. INTRODUCTION

Molecular monolayers at the water/air or water/oil interfaces have been investigated intensively for more than a century, starting with the pioneering works of Langmuir and Blodgett [1–5]. Not only do they provide an important manifestation of thermodynamics of two-dimensional (2D) systems, but they equally offer several interesting applications in nanolithography, micro patterning and optical coatings [6,7].

Related systems are monolayers of colloidal particles deposited at fluid/fluid interfaces. Much interest of the latter systems followed the seminal work of Pieranski [10], who found that sub-micron polystyrene spheres are trapped at the air/water interface and self-assemble into a 2D triangular lattice due to electrostatic repulsive interactions. More recently, a wide range of studies, including crystallization and aggregation of colloidal particles, have been performed on such colloidal monolayers [11–13].

Another key property of colloidal monolayers is their surface pressure/area isotherm. Such quantitive knowledge allows a direct control of particle spreading and self-assembling at the interface. The surface pressure can be used to fine tune the inter-particle spacing when the monolayer is deposited from an aqueous solution [14]. Furthermore, from measurements of inter-particle forces and the monolayer surface pressure, one can infer the magnitude of the effective colloidal charge [15–18], as this quantity is otherwise hard to measure.

Several approaches have been suggested for calculating the surface pressure [19–21]. Levental et al. [19] modeled a charged monolayer as a surface with continuous and uniform charge density, and calculated the electrostatic contribution to the surface pressure, denoted hereafter as $\Pi$. Using the nonlinear Poisson-Boltzmann (PB) theory yields a nonlinear expression for $\Pi$, expressed in terms of hyperbolic functions. This result, when treated within the linearized PB theory (the Debye-Hückel theory – DH, valid for strong electrolytes) yields a surface pressure that scales with $A$, the monolayer area, as $\Pi \sim A^{-2}$. In the opposite limit of weak electrolytes, however, the scaling is found to be $\Pi \sim A^{-1}$ [11]. Since the model is only valid for a uniform surface charge density, it is restricted to the close-packing limit of the colloids, where the monolayer surface charge can be considered as approximately uniform.

In the other limit of large inter-particle separation, Aveyard et al. [15] studied the surface pressure of a charged monolayer at the water/oil interface, and calculated $\Pi$ using a superposition of inter-particle forces. These forces can be explained as a consequence of trapped charges residing at the particle/oil surface (in contact with the oil phase), away from the oil/water interface. The charges induce opposite image charges inside the aqueous phase, as a way to satisfy the dielectric discontinuous jump at the water/oil interface. The monolayer in the dilute limit can be treated as a dipolar layer and yields a surface pressure that scales as $\Pi \sim A^{-3/2}$. We note that the same scaling law was found to be in agreement with their own experimental results [15].

The model by Aveyard et al. [15] mentioned above does not take into account the bulk concentration of ions in the aqueous sub-phase, and is a reasonable approximation only in the high-ionic strength (hence screened) limit. Moreover, as the model does not consider explicitly the distinct value of the dielectric constant of the colloidal monolayer, the dependence of $\Pi$ on the Debye screening length and monolayer dielectric constant have not been calculated.
Recently, Petkov et al. [16, 17] measured the monolayer surface pressure, Π, for charged silica particles deposited at the air/water interface. They calculated Π derived from the Maxwell stress tensor, employing the so-called Bakker formula [23]. The electrostatic field is assumed to vanish in the aqueous phase and was calculated in the air phase by postulating some specific ionic profiles at the surface. The surface charge density of each colloid and its accompanying screening was evaluated within a cell model, which is superimposed on a 2D square lattice. In the large inter-particle separation limit, it was found that the surface pressure scales as \( \Pi \sim A^{-3/2} \).

This scaling was shown to be in good agreement with experimental data [16, 17, 22] measured either in the absence of salt or for weak electrolytes, but contradicts the scaling law found earlier in Ref. [15]. Albeit the agreement between the model and experiment, the model was not derived in a self-consistent fashion. In particular, the use of the Bakker formula cannot be justified, because it relies on the homogeneity of the surface charge distribution, and the ionic profiles were postulated a priori to have a preset form. Furthermore, the ansatz used to express the screening resembles the form of a typical solution in the DH (strong electrolytes) theory, although the considered experimental regime (weak electrolytes) is clearly beyond the scope of this approximation.

Motivated by these different models, which yield distinct scaling forms (\( \Pi \sim A^{-\alpha} \), where \( \alpha = 1.2 \) [19], \( 5/2 \) [12] or \( 3/2 \) [16]), we present in this paper a different, more fundamental and self-consistent approach. The thermodynamic definition of the surface pressure is employed without the need to have any further assumptions other than using the linearized DH theory. Our calculation shows that for small inter-particle separation, the collective monolayer surface charge behaves as a continuum density, and the surface pressure scales as \( \Pi \sim A^{-2} \), in agreement with Ref. [19]. For large separation, the colloids show a dipole-like behavior, and the scaling becomes \( \Pi \sim A^{-5/2} \), recovering the results of Ref. [12]. Our model, therefore, agrees with the two limiting scenarios of colloidal packing of previous works [12, 19], and a smooth crossover between them. The theory derived herein also agrees well with available experimental data [15, 22] within the DH regime.

The present study addresses a generalized setup, where the colloidal monolayer has a finite thickness and an arbitrary value of the effective dielectric constant. We allow the colloidal charge distribution to be different on the water-side versus the air-side of the monolayer. The surface pressure is found to depend differently on the monolayer permittivity in the two limits of inter-particle separation. Furthermore, the dependence on the salt concentration can become non-monotonic for specific values of the charge density at the water-side. This finding is in contrast with the commonly employed assumption that the pressure depends solely on the charge located on the air-side of the colloids, for which the dielectric constant is much smaller, and when there is no screening.

The paper is organized as follows. In Section II, we derive a general formalism for calculating the surface pressure of arbitrarily charged surfaces within the DH theory. In Section III, we present the setup for the colloidal monolayer with a finite thickness and different charge distributions. The surface pressure is computed in Section IV, for a specific colloid charge distribution, and in Section V, we compare our findings to available experimental results. In Section VI, we discuss the surface pressure in the dilute and close-packing inter-particle separation limits, as well as its dependency on the ionic strength and monolayer dielectric constant. Finally, our conclusions are presented in Section VII.

## II. MONOLAYER SURFACE PRESSURE

We present a general framework for calculating the surface pressure of an arbitrarily charged interface coupled to a bulk ionic solution. The definition of the surface tension, \( \gamma \), is

\[
\gamma = \left( \frac{\partial F}{\partial A} \right)_{T,V},
\]

where \( F \) is the free energy of the system (comprising of an interface coupled with a bulk), and \( A \) is the overall surface area.

The surface pressure is related to the change in surface tension. For a charged monolayer, we can compare the surface tension with and without the charges

\[
\Pi = \gamma_0 - \gamma \equiv -\Delta \gamma_{el},
\]

where \( \gamma_0 \) and \( \gamma \) denote the surface tension in the absence and presence of surface charges, respectively. The electrostatic contribution to the surface pressure, \( \Pi \), is expressed in terms of \( \Delta f_{el} \), the change in electrostatic surface free-energy,

\[
\Pi = -\left( \frac{\partial}{\partial A} \int_A \Delta f_{el} \, d^2r \right)_{T,V}.
\]

The surface free-energy, \( \Delta f_{el} \), is defined as the amount of work (per unit area) needed to construct the surface. We introduce now the spatially averaged surface free-energy

\[
\langle \Delta f_{el} \rangle = \frac{1}{A} \int_A \Delta f_{el} \, d^2r,
\]

and write the surface pressure as

\[
\Pi = -\langle \Delta f_{el} \rangle - A \left( \frac{\partial \langle \Delta f_{el} \rangle}{\partial A} \right)_{T,V}.
\]

It is important to consider how the surface area is controlled in experiments. For monolayers comprising of a uniform surface density, two fundamentally different situations can occur, and they are known as the Gibbs monolayer and the Langmuir monolayer [2]. For Gibbs monolayers, the particles are soluble in the aqueous sub-phase.
The monolayer is an open system exchanging particles with the bulk, such that the chemical potential remains fixed. For a charged monolayer, it means that when the monolayer expands or contracts, its surface charge density remains constant, because the underlying physical properties that determine the surface coverage, such as the adsorption energy per unit area, approximately remain fixed. As a result, Δf_{el} is independent of the surface area and, Π = −Δf_{el}, by virtue of Eq. (7).

On the other hand, for Langmuir monolayers, the particles at the surface are completely insoluble in the water sub-phase, and the monolayer is a closed system with a fixed number of particles. The total charge, Q = \int_A σ d^2r, remains fixed, meaning that σ ∼ A^{−2}, even when the monolayer undergoes expansion or compression. For a uniformly charged surface and within the linear DH theory, the surface free-energy satisfies Δf_{el} ∼ A^{−2}, and from Eq. (6), Π = Δf_{el}.

Although these two simple cases may seem similar at first glance, the Gibbs and Langmuir monolayers yield an opposite relation between Π and Δf_{el}, as shown above. Clearly, these two extreme cases of uniform surface charge density are an over-simplification, and for non-uniform surface charge densities, the relation between Π and Δf_{el} becomes more intricate.

In the present study, we only consider the case of insoluble Langmuir monolayers, where the total charge (and particle number) of the monolayer is constant but the charge density (per unit area) can vary. Our approach is general and enables us to calculate Π for any configuration of surface charges. The charged surface is coupled to an electrolyte solution, and Δf_{el} is calculated using the Poisson-Boltzmann (PB) theory. The water and air phases are treated as two continuum media with dielectric constants, \varepsilon_w and \varepsilon_a, respectively. The mobile ions in the aqueous solution are taken to be point-like, yielding the well-known PB equation for a monovalent 1:1 electrolyte

\[ \nabla^2 \psi = \frac{2e \sigma_b}{\varepsilon_0 \varepsilon_w} \sinh \left( \frac{e \psi}{k_B T} \right), \]  

(6)

where ψ is the electrostatic potential, e the elementary charge, \varepsilon_0 the vacuum permittivity, \varepsilon_w the relative permittivity of water, n_b the bulk concentration of the electrolyte and k_B T the thermal energy.

For a surface with surface charge σ separating an aqueous solution from the air (or oil), the electrostatic boundary condition is

\[ \hat{n} \cdot \left[ \varepsilon^-_f \nabla \psi^- - \varepsilon^+_i \nabla \psi^+ \right] \sigma \varepsilon_0, \]  

(7)

where \hat{n} denotes the unit vector normal to the surface. The ± superscripts denote the external (+) and internal (−) regions with respect to the surface, and the direction of \hat{n} is chosen to point from inside toward the outside.

From the well known charging method, the electrostatic free-energy due to the presence of an electric double layer can be evaluated as

\[ \Delta f_{el} = \int_0^\infty \psi_b(\sigma') d\sigma'. \]  

(8)

Equations (11) through (8) are sufficient to obtain the surface pressure in the most general case. However, for simplicity, the Debye-Hückel (DH) linearization scheme can be employed for Eq. (6),

\[ \nabla^2 \psi = \kappa^2_D \psi, \]  

(9)

for cases when ψ ≪ k_B T/e. In the above equation, the inverse Debye screening length is \kappa_D = \sqrt{8 \pi n_b e^2}, and the Bjerrum length \lambda_B = e^2/(4 \pi \varepsilon_0 \varepsilon_w k_B T) is about 0.7 nm in water (\varepsilon_w ≈ 78) at room temperature.

In the DH regime, ψ_b and σ are related linearly, and Eq. (8) becomes

\[ \Delta f_{el} = \frac{1}{2} \psi_b \sigma. \]  

(10)

This formula can be generalized for two charged surfaces, \sigma_i, \ i = 1, 2, each with surface potential, \psi_{s,i}, and surface charge, \sigma_i,

\[ \Delta f_{el} = \frac{1}{2} \sum_{i=1,2} \psi_{s,i} \sigma_i. \]  

(11)

Eq. (11) is obtained by the linearization of the expression presented in Ref. [29], in the context of two interacting charged surfaces. In the following section, the above equation will be used to calculate the free energy for Langmuir monolayers that are modeled as two charged interfaces separated by a dielectric layer.

III. MODELING OF THE COLLOIDAL MONOLAYER

The charged colloidal monolayer is schematically depicted in Fig. 1. It is located at the interface between a dielectric medium of dielectric constant \varepsilon_a (non-aqueous medium such as air or oil) on its top side, and a monovalent 1:1 electrolyte solution, of dielectric constant \varepsilon_w, on its bottom side. The monolayer itself is treated as a continuum medium with finite thickness, d, and a dielectric constant, \varepsilon_c. Each colloidal charge is modeled as a patch of surface charge, located at the air-side and water-side of the particle, with different values assigned to each side.

1 Although the above charging method takes into account the entropy of the mobile ions in the solution, it does not include the entropy of the surface charges. In our model, those charges originate from the charge distribution on large colloidal particles, forming a monolayer at the air/water interface. However, since the colloids are considered as macro-particles, this entropy contribution can be ignored.
FIG. 1: (color online) Schematic drawing of the colloidal monolayer in between two interfaces: a top one, at \( z = 0 \), in contact with air (dielectric constant \( \varepsilon_a \)), and a bottom one, at \( z = -d \), in contact with an aqueous solution having dielectric constant \( \varepsilon_w \), and Debye screening length, \( \kappa_D^{-1} \). (a) The layer of finite thickness, \( d \), is modeled as a dielectric layer of dielectric constant \( \varepsilon_c \), spread between the water and air phases. The colloidal charges accumulate on the water-side and air-side, and form a square lattice with lattice constant \( L \). The two corresponding surface charge densities are denoted, respectively, as \( \sigma_a \) and \( \sigma_w \). (b) Cross section of the monolayer. The colloid charge density is spread over the colloid diameter \( D \), and the distance between colloid centers is \( L \).

In order to calculate the surface pressure, we need to evaluate first the electrostatic potential. The potential in the air phase, \( \psi^{(a)} \), as well as inside the colloidal monolayer region, \( \psi^{(c)} \), satisfies the Laplace equation,

\[
\nabla^2 \psi^{(a)} = 0, \quad \nabla^2 \psi^{(c)} = 0, \quad (12)
\]

while the potential in the aqueous phase, \( \psi^{(w)} \), satisfies the DH equation, Eq. (9)

\[
\nabla^2 \psi^{(w)} = \kappa_D^{-2} \psi^{(w)}, \quad (13)
\]

and depends on the solution ionic strength via the Debye screening length, \( \kappa_D^{-1} \).

As mentioned above, the charges on the colloidal monolayer are modelled by two parallel and charged layers. The first located on the air-side (\( z = 0 \)) and the second on the water-side (\( z = -d \)). The monolayer itself is constructed by repeating the surface charge patches (each representing an individual colloid) on a 2D periodic square lattice with lattice parameter \( L \), as is seen in Fig. 1. Note that the patches can have an arbitrary shape and charge distribution with typical length scale, \( D < L \). For an arrangement on a square lattice, the surface charge densities on the monolayer air-side and water-side, \( \sigma_a(x, y) \) and \( \sigma_w(x, y) \), are periodic functions in \( x \to x + L \) and \( y \to y + L \).

The boundary conditions at the \( z = 0 \) and \( z = -d \) planes are obtained from Eq. (7),

\[
\varepsilon_c \frac{\partial \psi^{(c)}}{\partial z} \bigg|_{z=0^+} - \varepsilon_a \frac{\partial \psi^{(a)}}{\partial z} \bigg|_{z=0^-} = \frac{1}{\varepsilon_0} \sigma_a(x, y),
\]

\[
\varepsilon_w \frac{\partial \psi^{(w)}}{\partial z} \bigg|_{z=-d^+} - \varepsilon_c \frac{\partial \psi^{(c)}}{\partial z} \bigg|_{z=-d^-} = \frac{1}{\varepsilon_0} \sigma_w(x, y), \quad (14)
\]

and at infinity we demand that the electrostatic field vanishes, \( \text{i.e.}, \lim_{z \to \pm \infty} |\nabla \psi| = 0 \). The two periodic charge densities, \( \sigma_a(x, y) \) and \( \sigma_w(x, y) \), can be expressed by their 2D Fourier series

\[
\sigma_a(r) = \frac{1}{L^2} \sum_{n,m = -\infty}^\infty \hat{s}_a(k)e^{i k \cdot r},
\]

\[
\sigma_w(r) = \frac{1}{L^2} \sum_{n,m = -\infty}^\infty \hat{s}_w(k)e^{i k \cdot r}, \quad (15)
\]

where \( r = (x, y) \) is the 2D in-plane vector. For a square lattice, the integer numbers \( \{n, m\} = 0, \pm 1, \pm 2, \ldots \), parameterize the discrete \( k \)-vector of the reciprocal space with \( k = 2\pi/(L\sqrt{n^2 + m^2}) \), and \( \hat{s}_i(k), i = a, w, \) is the \( k \)-component of the Fourier transform of a single colloid charge distribution (\( i.e. \), within the unit cell).

The surface potentials evaluated at the top and bottom surfaces, \( \psi_a^{(s)} \) and \( \psi_w^{(w)} \), can also be written in terms of their Fourier components:

\[
\psi_s^{(i)}(r) = \sum_{n,m = -\infty}^\infty \tilde{\psi}_s^{(i)}(k)e^{i k \cdot r}, \quad (16)
\]

with \( i = a, w \), while \( \tilde{\psi}_s^{(i)}(k) \) denotes the Fourier coefficients of \( \psi_s^{(i)}(r) \).

A linear relation between the surface potential and surface charge density will emerge from the boundary conditions as our model is linear. Similar to the notation used in Eq. (11) and in Appendix A, the generalized linear response is written in Fourier space as,

\[
\tilde{\Psi}_s(k) = \frac{1}{L^2} C^{-1}(k) \tilde{\Sigma}(k), \quad (17)
\]

where in a compact notation, \( \tilde{\Psi}_s(k) = (\tilde{\psi}_a^{(s)}(k), \tilde{\psi}_w^{(w)}(k)) \) and \( \tilde{\Sigma}(k) = (\tilde{s}_a(k), \tilde{s}_w(k)) \) are vectors, and \( C(k) \) is a \( 2 \times 2 \) matrix. The diagonal components of the \( C(k) \) matrix are the differential capacities (per unit area) of the ‘a’ and
‘w’ surfaces, while the off-diagonal ones represent cross-capacitive terms between the two surfaces.

Next, as the colloidal arrangement is periodic, the spatial average over the surface free energy [Eq. 14] can be taken over a single lattice cell of area $L^2$. Hereafter, we shall omit the bracket notation from $(\Delta f_{el})$ for the sake of simplicity, but the free energy is always averaged over one unit cell. Using the Parseval theorem, this quantity is equal to a summation over the reciprocal lattice vector $\mathbf{k}$, given by

$$\Delta f_{el} = \frac{1}{2L^2} \sum_{\mathbf{k}} \hat{\Sigma} C^{-1} \hat{\Sigma},$$  \hspace{1cm} (18)

Adopting the notation of Refs. [16, 17], we introduce a dimensionless parameter, $0 \leq \xi \equiv D/L \leq 1$, which is the ratio between the particle diameter, $D$, and the inter-particle separation, $L$. The limit $\xi \ll 1$ denotes the dilute monolayer density $(D \ll L)$, while $\xi \to 1$ corresponds to the close-packing limit $(D \simeq L)$. Using $\mathbf{k} = 2\pi/(L\sqrt{n^2 + m^2})$ and the dimensionless $\xi$, the above summation is written as

$$\Delta f_{el} = 2\xi^2 G(\xi),$$  \hspace{1cm} (19)

where the function $G(\xi)$ is defined as

$$G(\xi) = \frac{\xi^2}{D^4} \sum_{n,m=0}^{\infty} \theta_{nm} (\Sigma C^{-1} \Sigma)_{nm},$$  \hspace{1cm} (20)

and

$$\theta_{nm} = (2 - \delta_{n0})(2 - \delta_{m0})/4,$$

depends on the Kronecker delta function, $\delta_{nm}$, where we made use of the square lattice symmetry of our setup.

Finally, from Eqs. [5] and [19]-[20], the surface pressure is given by

$$\Pi(\xi) = \frac{3}{4} G(\xi).$$  \hspace{1cm} (21)

Equation (21) is the general expression for the surface pressure for our model. Furthermore, the framework provided above can be generalized for any model within the DH approximation. In the following section, we will use this result for a specific choice of the charge distribution.

IV. RESULTS

In order to calculate $\Pi(\xi)$ of Eq. (21), one has to evaluate the derivative of $G(\xi)$ from Eq. (20). The function $G(\xi)$ depends on the details of the surface charge distribution of a single colloid, $s(r)$, as well as on the boundary conditions. We proceed by assuming that $s(r)$ is a radial symmetric function and has a separate Gaussian form on the ‘a’ and ‘w’ sides of the monolayer

$$s(r) = \frac{2Q}{\pi D^2} \exp \left( -\frac{r^2}{D^2} \right).$$  \hspace{1cm} (22)

where $r = |r|$, and $Q = Q_a$ or $Q_w$ is the charge on the ‘a’ or ‘w’ sides, respectively. This, in turn, leads to a Fourier transform of $s(r)$, which also has a Gaussian form,

$$\tilde{s}(n\xi, m\xi) = Q \exp \left[ -\frac{\pi^2}{2} \xi^2 l_{nm}^2 \right],$$  \hspace{1cm} (23)

where $l_{nm} = \sqrt{n^2 + m^2}$.

The explicit solution for the electrostatic potential profile in the three spatial regions (‘a’, ‘c’ and ‘w’) and the capacitance matrix are given in Appendix A. Based on these solutions, the function $G(\xi)$ is written as

$$G(\xi) = \frac{g(0)}{4} \xi^2 + \xi^2 \sum_{n=1}^{\infty} g(\xi n_{0}),$$  \hspace{1cm} (24)

and

$$g'(0) = \frac{\varepsilon_a 2\pi d^2}{\varepsilon_c \varepsilon_0 D^3} \left[ Q_a + \frac{\varepsilon_a \varepsilon_c Q_a + Q_w}{\varepsilon_w \kappa_D D} \right]^2.$$  \hspace{1cm} (26)

We will use $g(0)$ and $g'(0)$ in order to evaluate the surface pressure analytically in the close-packing ($\xi = D/L \to 1$) and dilute ($\xi = D/L \ll 1$) limits.

A. Close-packing colloid limit, $\xi \to 1$

In the close-packing limit, $\Pi$ can be derived analytically by investigating $G(\xi)$ and its derivative in the $\xi = D/L \to 1$ limit. The dominant contribution to Eq. (21) originates from the first term, since a simple substitution of $\xi \to 1$ in Eq. (21) implies that the contributions from the two remaining series are exponentially small, approximately of order $\exp (-\pi^2) \sim 10^{-5}$, and can be safely neglected. Then, from Eqs. (24) and (25) one can derive

$$G(\xi) \simeq \frac{1}{4} \left[ \frac{Q_a^2 d}{\varepsilon_c \varepsilon_0} + \frac{(Q_a + Q_w)^2}{\varepsilon_c \varepsilon_0 \kappa_D D} \right] \frac{\xi^2}{D^2},$$  \hspace{1cm} (27)

and the value of $\Pi$ for $\xi \ll 1$ is given by Eqs. (21) and (21)

$$\Pi \simeq \left[ \frac{Q_a^2 d}{2\varepsilon_c \varepsilon_0} + \frac{(Q_a + Q_w)^2}{2\varepsilon_0 \varepsilon_w \kappa_D D} \right] \frac{1}{A^2}.$$  \hspace{1cm} (28)

where we substituted $(\xi/D)^4 = L^{-4} = A^{-2}$ in Eq. (28). Therefore, in the close-packing limit, the surface pressure scales as $A^{-2}$, and is consistent with the continuum
limit of the monolayer surface charge. As the colloids approach each other, their double-layers overlap and resemble the response to a uniform surface charge density at the air/water interface.

B. Dilute colloid limit, $\xi \ll 1$: an effective dipolar monolayer

For the dilute limit, $\xi = D/L \ll 1$, we remark that $G(\xi)$ has the form of a Riemann sum [38]. Using the Euler-Maclaurin formula (see Appendix B), we expand $G(\xi)$ to leading orders

$$G(\xi) \simeq \int_0^{\pi/2} d\theta \int_0^\infty g(\rho) \rho d\rho - \frac{g'(0)}{18} \xi^3.$$  

(29)

Using Eqs. (21), (26) and (29), the value of $\Pi$ in the dilute limit is obtained as

$$\Pi(\xi) = \frac{\pi \varepsilon_a}{3 \varepsilon_c \varepsilon_0} \frac{d^2}{A^5} \left[ Q_a + \frac{\varepsilon_c}{\varepsilon_w} Q_a + Q_w \kappa_D d \right]^2 \left( \frac{\xi}{D} \right)^5.$$  

(30)

The surface pressure in Eq. (30) scales as $(\xi/D)^5 = A^{-5/2}$ for $\xi \ll 1$. This dilute-limit result stems from effective dipole-dipole interactions between the colloids, primarily mediated by the air phase. Indeed, by substituting $(D/\xi)^2 = A$ and after some rearrangements, we find

$$\Pi = \frac{\pi}{12} \frac{p_{\text{eff}}^2}{\varepsilon_0 \varepsilon_a} \frac{1}{A^{5/2}} + O \left( \frac{1}{A^{7/2}} \right),$$  

(31)

where the effective dipole moment $p_{\text{eff}}$ is written as the sum of two terms,

$$p_{\text{eff}} = p_1 + p_2 = \frac{2 \varepsilon_a}{\varepsilon_c} Q_a d + \frac{2 \varepsilon_a}{\varepsilon_w} Q_a + Q_w \kappa_D d.$$  

(32)

In Appendix C, we calculate $\Pi$ in the dilute limit directly from the dipole-dipole interaction energy. This calculation suggests that the dilute limit, as in Eqs. (31)- (32), is independent of the specific functional form of the surface charge density. One might indeed expect this behavior as the inter-particle distance satisfies $D \ll L$, and the details of the colloidal charge distribution are washed out.

For a given inter-particle separation $L$, we express the dependence of $\Pi$ on the ionic strength using Eqs. (31)- (32),

$$\Pi = \left[ 1 + \left( 1 + \frac{Q_w}{Q_a} \right) \frac{\varepsilon_c}{\varepsilon_w} \frac{1}{\kappa_D d} \right]^2 \Pi_\infty,$$  

(33)

where $\Pi_\infty = \Pi(\kappa_D d \rightarrow \infty)$ is the surface pressure for a vanishing screening length. From Eq. (33), we deduce that for $Q_w/Q_a > 0$, $\Pi$ is a monotonic function of the Debye screening length, and converges to $\Pi_\infty$, for very high electrolyte concentrations.

However, if the ratio $Q_w/Q_a$ becomes negative, $\Pi$ might even vanish for certain values of $\kappa_D$, as can be seen in Fig. 2 for a specific choice of $Q_w/Q_a = -100$. Moreover, $\Pi$ is non-monotonic with respect to the salt concentration. This presents a compelling evidence that surface charges on both sides of the colloid particle can play a role in determining the magnitude of $\Pi$. We shall further discuss this observation below.

We conclude this subsection by noting that there are two separate cases for the effective dipole moment, Eq. (32): (i) for strong electrolytes, where $\kappa_D d \gg (1 + Q_w/Q_a) (\varepsilon_c/\varepsilon_w)$, $p_{\text{eff}}$ is approximated as

$$p_{\text{eff}} \simeq p_1 = \frac{2 \varepsilon_a}{\varepsilon_c} Q_a d.$$  

(34)

Here $p_{\text{eff}}$ mainly depends on $p_1$, since the air-exposed charge induces an image charge in the aqueous phase, with a charge separation distance of $2(\varepsilon_a/\varepsilon_c)$. (ii) For weak electrolytes, namely, $\kappa_D d \ll (1 + Q_w/Q_a) (\varepsilon_c/\varepsilon_w)$, $p_{\text{eff}}$ is well approximated by the second term, $p_2$,

$$p_{\text{eff}} \simeq p_2 = \frac{2 \varepsilon_a}{\varepsilon_w} (Q_a + Q_w) \kappa_D^{-1}.$$  

(35)

The relevant charge determining the dipole moment is the net charge on both sides of the particle, as a result of the electro-neutrality due to screening. The charge separation is then proportional to the screening length.
FIG. 3: (color online) Rescaled surface pressure, \( \Pi/\Pi_0 \) (green solid line), and rescaled surface free-energy, \( \Delta f_{el}/\Delta f_0 \) (blue dashed line), plotted on a log-log plot as a function of \( \xi \). The rescaling is done with respect to the close-packing values: \( \Pi_0 = \Pi(\xi = 1) \) and \( \Delta f_0 = \Delta f_{el}(\xi = 1) \). The free energy and pressure scale identically as \( \sim \xi^4 \) in the \( \xi \to 1 \) limit, where the monolayer can be regarded as a having a uniform surface charge. In the dilute limit (\( \xi \ll 1 \)), however, \( \Pi \sim \xi^3 \), and differs significantly from \( \Delta f_{el} \sim \xi^2 \).

C. The general \( \xi \) case

The surface pressure, \( \Pi \), of Eq. (21), can be calculated numerically for any intermediate value of \( \xi \). We limit ourselves to the more common case of strong electrolytes, \( \kappa_D d \gg (1 + Q_w/Q_a)(\varepsilon_c/\varepsilon_w) \), with \( Q_w = 0 \), \( d = D \) and \( \kappa_D d = 10 \). We have chosen \( Q_w = 0 \) on the water side, without loss of generality, because it merely sets the strong electrolyte regime to \( \kappa_D d \gg \varepsilon_c/\varepsilon_w \).

The function \( G(\xi) \) is calculated by summing one hundred terms of the two series in Eq. (20), where their explicit form is given in Appendix A. Choosing a Gaussian form for \( s(\rho) \), the colloid charge distribution of Eq. (22) yields a better convergence of the series for small values of \( \xi \), as compared with \( s(\rho) \) for a uniform charge distribution on each colloid. The space-averaged surface free-energy, \( \Delta f_{el} \), can be calculated via Eq. (19), and the function \( \Pi(\xi) \) is evaluated via Eq. (21), by taking numerically the first derivative of \( G(\xi) \).

The quantities \( \Delta f_{el} \) and \( \Pi \), rescaled by their maximal values at \( \xi = 1 \) (\( \Pi_0 \) and \( \Delta f_0 \), respectively), are shown in Fig. 3 on a log-log plot. Clearly, both coincide in the close-packing limit (\( \xi \lesssim 1 \)), where the continuum limit holds, i.e., \( \Pi \simeq \Delta f_{el} \sim \xi^4 \sim A^{-2} \). However, in the dilute regime (\( \xi \ll 1 \)), the surface free-energy and surface pressure differ considerably as \( \Delta f_{el} \sim \xi^2 \) and \( \Pi \sim \xi^3 \).

A plot of \( \Pi \), rescaled by its maximal value, is given in Fig. 4 for different values of the monolayer dielectric constant, \( \varepsilon_c = 1, 2, 4 \) and 8. The variation of the rescaled surface pressure with \( \varepsilon_c \) is quite substantial only in the dilute-packing limit, where it varies as \( 1/\varepsilon_c \), as is implied by Eq. (20). We note that \( \Pi_0 \) (the rescaling prefactor) is the close-packing value of \( \Pi \), \( \Pi_0 = \Pi(\xi = 1) \), and is by itself proportional to \( 1/\varepsilon_c \), [see Eq. (28)].

V. COMPARISON TO EXPERIMENTS

It would be of value to compare our theoretical predictions to previous experiments. In Refs. [15] and [22], the surface pressure of charged polystyrene latex particles is measured at octane/water and decane/water interfaces, respectively. The fit to these experimental data shown in Fig. 5 employs the full expression as prescribed in Eqs. (21), (24) and (A4)-(A5), and uses a single fit parameter, which is the air-exposed surface charge of a single colloid, \( \sigma_a = Q_a/\pi(D/2)^2 \).

In general, there are two fit parameters, \( \sigma_a \) and \( \sigma_w \). However, we observe that the experiments considered here [15, 22] used intermediate to high salt concentrations. Thus, \( \kappa_D^{-1} \lesssim 1 \) nm is much smaller than the colloid particle size \( D \geq 1 \mu m \), and \( \varepsilon_w \ll \varepsilon_w \) for the two bounding media. It is then justified to neglect \( \sigma_w \) in this case, since the contribution from the water charges becomes much smaller (see Section VI for more details). We also find that employing \( \sigma_w \) as a second fit parameter makes no substantial difference in this case. Nevertheless, there might exist physical scenarios where the assumption \( \sigma_w = 0 \) is inaccurate (as is discussed below).

Figure 5a presents the fit with the data of Ref. [15]. The data corresponds to an experimental setup with a 10 mM NaCl solution, and particles of diameter \( D = 2.6 \mu m \). The resulting air-exposed surface charge \( \sigma_a \) is obtained as a fit parameter, \( \sigma_a = 870 \mu C/m^2 \simeq 5 \times 10^{-5} \mu C/m^2 \).
10^{-3} \epsilon/nm^2$, which is a reasonable surface charge density. We set the layer thickness $d$ to be equal to the particle diameter $D$, thus, ignoring effects of colloid immersion in the aqueous phase due to wetting. The dielectric permittivities were taken to be $\varepsilon_w = 80$, $\varepsilon_c = 2.5$ and $\varepsilon_{oil} = 2$ for the water, polystyrene latex beads and oil (decane or octane) phases, respectively. This represents a good fit in the intermediate ionic strength regime.

In a similar fashion, Fig. 5b shows multiple fits to the data of Ref. [22]. The surface pressure was measured for different aging times, by varying the exposure time of the monolayer in contact with 250 mM NaCl solution, between 2, 19 and 115 hours. As was mentioned in Ref. [22], the number of dissociated groups on the colloid surface, corresponding to the surface charge, diminishes with time. Hence, Fig. 5b shows a decrease of the surface pressure with aging time. The colloid diameter was set to $D = 3.1 \mu m$, and for aging times of 2, 19 and 115 hours, the fits correspond to $\sigma_a = 720$, 650 and 530 $\mu C/m^2$, respectively (charge densities of a few electrons per thousand nm$^2$). As seen in Fig. 5 our model yields good agreement with experiments, and the fits become even better for stronger electrolytes (Fig. 5b), as one might expect from the DH approximation.

Figure 6a shows measurements done in the strong electrolyte case and mainly in the close packing regime [22]. The prediction of the close-packing power law, $\Pi \sim A^{-2}$, follows quite well the data points. On the contrary, Fig. 6b shows that in the absence of salt, the measurements done in Ref. [22] and by Petkov et al. [10] exhibit a different scaling, $\Pi \sim A^{-3/2}$. This result is beyond the scope of the present theory that employs the DH approximation.

VI. DISCUSSION

Scaling laws derived from the analytical results for the surface free-energy and surface pressure are obtained in two limits (see Fig. 3): (i) the dilute limit ($\xi = D/L \ll 1$), Eq. (31); and, (ii) the close-packing limit ($\xi = D/L \lesssim 1$), Eq. (28).

In the dilute limit, we have found that the surface pressure can be described in terms of dipole-dipole interactions, where the effective dipole moment $p_{eff}$, Eqs. (34)-(35), arises from ionic screening in the aqueous phase. The charge separation corresponding to this dipole moment, $p_{eff} = p_1 + p_2$, is given in terms of the colloid thickness $d$, for $p_1$ [Eq. (34)] in the strong electrolyte limit, or in terms of the Debye screening length for $p_2$ [Eq. (35)], in the weak limit. The sum of these two contributions, $p_1 + p_2$, constitutes the effective dipole moment of each colloid. This description is valid for intermediate cases, and demonstrates an explicit dependence on the monolayer dielectric permittivity and the subphase ionic strength. We note that previous works [15, 32, 33] derived less general results for the dilute limit, with either

---

\[ \sigma_a = 720, 650 \text{ and } 530 \mu C/m^2 \]
The measurements were taken in the close-packing limit and in the high-salt regime, where the DH approximation holds, for aging times between 2-115 hours. For all aging times, the expected power law of \( A \) agrees well with the data. (b) Data adapted from Vermant et al. [22] (main figure) and Petkov et al. [16] (inset). Without added salt, a different power law of \( A^{-3/2} \) agrees with the data of the same authors [22] (main figure). Measurements performed by Petkov et al closer to the dilute limit and with no added salt also agree with the \( A^{-3/2} \) power law (inset).

\[ p = p_1 \text{ or } p = p_2 \text{ (and only for } Q_a = 0) \text{.} \]  

The colloidal monolayer permittivity strongly affects the surface pressure \( \Pi \) through the magnitude of \( p_1 \), Eq. [44]. The rescaled surface pressure \( \Pi/\Pi_0 \) of Fig. 4 scales as \( 1/\varepsilon_c \) in the dilute-packing limit, implying that \( \Pi \sim 1/\varepsilon_c^2 \) [see Eq. (28)]. However, in the close-packing limit, the rescaled surface pressure is independent of \( \varepsilon_c \); hence, \( \Pi \sim 1/\varepsilon_c \). The latter observation stems from the difference between the two regimes: dipole-dipole interactions vs. a uniform electric double layer.

Several comments can be made on the salt effects. First, for strong electrolytes, the surface pressure is nearly independent of ionic strength. This result is consistent with experimental findings of a weak dependence of the inter-particle force and surface pressure on salt concentration [15, 31]. An exception occurs when \( Q_w \) and \( Q_a \) have opposite signs. For example, in Fig. 2 we plot the dependence of \( \Pi \) on \( \kappa_D \) and show that it is non-monotonic and even vanishes for a specific salt concentration.

The dependence on salt is quite different for weak electrolytes. A clear divergence of the surface pressure is observed for very weak ionic strength. We remark that Eq. (33) might become inaccurate in this limit, since the validity of the DH approximation breaks down for high surface charges and weak electrolytes. In this case, it may be more appropriate to consider methods other than the DH approximation [32, 34, 35].

We would like to pay special attention to the charge on the water-side, \( Q_w \). Although it was conveniently set to zero in Fig. 5 nevertheless we find that \( Q_w \) can, in certain cases, affect the surface pressure. Since the energetic cost of charging a surface in contact with a low dielectric material is high, it is commonly believed [16, 18, 32] that ions from the water phase prefer to diffuse to the air-side of the layer. These ions neutralize some of the air-side charges reducing their net charge. As a result, the water-facing charge \( Q_w \) can become much higher than \( Q_a \).

In contrast to previous theoretical derivations [15, 16, 18, 31, 30], which a priori neglected \( Q_w \), we can compare the contributions to the surface pressure from charges located at the top and bottom sides of the monolayer. For example, in the dilute limit (\( \xi \to 0 \)), we calculate separately the surface pressure that results from charges residing only on the colloid/air interface (\( \Pi_{ca} \) for \( Q_w = 0 \)), and for the opposite case, when they reside only on the colloid/water interface (\( \Pi_{cw} \) for \( Q_a = 0 \)). The ratio between the two is given by:

\[
\lim_{\xi \to 0} \frac{\Pi_{ca}}{\Pi_{cw}} = \left( \frac{Q_a}{Q_w} \right)^2 \left( 1 + \frac{\varepsilon_w}{\varepsilon_c} \kappa_D d \right)^2 . \tag{36}
\]

Clearly, the contribution of the water-side charges cannot be neglected when the surface charge residing on the air-side is much smaller than the one on the water-side. The corresponding \( Q_s/Q_w \) ratio is estimated to be quite large. For example, this ratio can be \( 200 - 2000 \) for a 1 mM ionic aqueous solution at room temperature and for silica particles of diameter \( D = 0.1 - 1 \mu m \). This scenario might be achieved in some setups. Using the same logic, a similar conclusion may also be drawn for the close-packing limit.
In this work we study the surface pressure of a monolayer composed of charged colloids at the air/water interface, within the linear PB theory (DH theory). The colloidal monolayer is treated as a continuum dielectric, with dielectric constant $\varepsilon_c$ and finite thickness $d$, separating two phases: an electrolyte solution and air (or oil), with $\varepsilon_w \gg \varepsilon_a$. Charges of the colloidal particles facing the water-side and air-side are modeled as surface charge patches superimposed on a 2D square lattice. As was previously suggested for similar setups \cite{20, 21}, the presence of charged particles at the air/water interface results in an excess of surface free-energy, and the surface pressure can be calculated directly from the latter [see Eq. (11)].

Although the exact solution of the surface pressure requires a numerical summation of many terms in Eq. \[\text{(21)}\] (see Fig. [3]), the scaling forms are obtained analytically, yielding for the close-packing limit ($\xi \equiv D/L \to 1$), $\Pi \sim \xi^4 \sim A^{-2}$ and for the dilute limit ($\xi \ll 1$), $\Pi \sim \xi^4 \sim A^{-5/2}$. The former is consistent with the uniform surface charge density \cite{11, 21, 30}, while the latter can be viewed as originating from dipolar interactions between discrete dipoles \cite{15, 32} (see also Appendix C).

The effective dipole moment, $p_{\text{eff}}$, of the charged colloids is calculated analytically, and is found to depend on the ionic strength (Fig. [2]), the dielectric properties of the colloidal particles (Fig. [1]), and the amount of charges residing on the water-side ($Q_w$) and air-side ($Q_a$) of the colloid. We detail physical conditions for which the contribution of the water-side charges to the surface pressure is not small, in contrast to the common belief. In addition, the dependence on salt concentration is explored. For close-packing and dilute colloid limits, the monolayer permittivity ($\varepsilon_c$) is shown to affect the surface pressure in different ways.

Our model agrees well with available experimental data (Fig. [5]), and explains the physical behavior for strong electrolytes ($\Pi \sim A^{-2}$ in the close-packing limit). However, some experimental results \cite{16, 17, 22} exhibiting longer-ranged interactions ($\Pi \sim A^{-3/2}$) for weak electrolytes are yet poorly understood. In addition, a previous work \cite{19} hints that the proper scaling in the no-salt regime for uniform surface charge can become as weak as $\Pi \sim A^{-1}$. We hope that our study, restricted to the DH regime, will stimulate even further theoretical and experimental investigations, which will hopefully shed light on the abnormal surface pressure scaling of charged colloidal monolayers in the no-salt regime.

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VII. CONCLUSIONS

We present the explicit calculation of the electrostatic potential in the various spatial regions for our model as depicted in Fig. 4. Using the same notations introduced earlier, $\psi(\mathbf{r}, z)$ is the $(n, m)$ spatial mode of $\psi(\mathbf{r}, z)$, with the wavevector $k_{nm} = 2\pi/(Ll_{nm})$ where $l_{nm} = \sqrt{n^2 + m^2}$. For clarity sake, we omit the $(n, m)$ subscripts from the $k_{nm}$ and refer to the $(n, m)$ Fourier mode simply as $k$. Denoting the potential in the top air phase, middle colloidal monolayer and bottom water phase as $\tilde{\psi}(a)$, $\tilde{\psi}(c)$ and $\tilde{\psi}(w)$, respectively, the potential $\tilde{\psi}(k, z)$ in the three spatial regions is obtained from Eqs. \[\text{(12)}\]-\[\text{(16)}\]:

\[
\begin{align*}
\tilde{\psi}(a)(k, z) &= \tilde{\psi}(a)(k) \exp(-\Lambda_{nm}z), \\
\tilde{\psi}(w)(k, z) &= \tilde{\psi}(w)(k) \\
&\quad \times \exp \left(\left(\Lambda_{nm}^2 + \kappa_D^2\right)^{1/2}(z + d)\right), \\
\tilde{\psi}(c)(k, z) &= \tilde{\psi}(c)(k) \sinh(\Lambda_{nm}(z + d)) \\
&\quad \frac{\sinh(\Lambda_{nm}d)}{\sinh(\Lambda_{nm}d)},
\end{align*}
\]

with $\Lambda_{nm} \equiv 2\pi x_l_{nm}/D = 2\pi l_{nm}/L$. It is easy to see that the potential $\tilde{\psi}$ given in Eq. \[\text{(A1)}\] is continuous at the $z = 0$ and $z = -d$ boundaries, where it is equal to $\tilde{\psi}(a)$ and $\tilde{\psi}(w)$, respectively.

The next step is to obtain the inverse capacitance matrix, $C^{-1}(n\xi, m\xi)$, introduced in Eq. \[\text{(17)}\]. Using the boundary conditions, Eq. \[\text{(14)}\], we obtain for the four matrix elements $C_{ij}^{-1}$:

\[
\begin{align*}
C_{11}^{-1} &= \frac{1}{c_{nm}} \left[ 1 + \frac{\varepsilon_w}{\varepsilon_c} \sqrt{1 + (\kappa_D/\Lambda_{nm})^2} \tanh(\Lambda_{nm}d) \right], \\
C_{22}^{-1} &= \frac{1}{c_{nm}} \left[ 1 + \left(\frac{\varepsilon_a}{\varepsilon_c}\right)^2 \tanh(\Lambda_{nm}d) \right], \\
C_{12}^{-1} &= C_{21}^{-1} = \frac{1}{c_{nm}} \left[ \frac{1}{\cosh(\Lambda_{nm}d)} \right],
\end{align*}
\]

with

\[
\begin{align*}
c_{nm} = &\varepsilon_0 \varepsilon_w \Lambda_{nm} \left[ \sqrt{1 + (\kappa_D/\Lambda_{nm})^2} + \frac{\varepsilon_a}{\varepsilon_w} + \left(\frac{\varepsilon_a}{\varepsilon_c} \sqrt{1 + (\kappa_D/\Lambda_{nm})^2} + \varepsilon_c/\varepsilon_w\right) \tanh(\Lambda_{nm}d) \right] (A3)
\end{align*}
\]

Appendix A: Derivation of the Electrostatic Potential

Potential

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Potential

Potential
for the \((n,m)\) modes. Using the above expressions and Eq. (19), Eq. (24) of Section IV is obtained,

\[
g(\rho) = \frac{1}{2\pi D^2 \varepsilon_0 \varepsilon_w \rho h(\rho)} e^{-\rho^2} \\
\times \left( Q_a^2 \left[ 1 + \frac{\varepsilon_w}{\varepsilon_c} \sqrt{1 + (\kappa_D D/2\pi \rho)^2} \tanh (2\pi \rho d/D) \right] \\
+ Q_c^2 \left[ 1 + \frac{\varepsilon_c}{\varepsilon_w} \tanh (2\pi \rho d/D) \right] \\
+ \frac{2Q_c Q_w}{\cosh (2\pi \rho d/D)} \right),
\]

(A4)

where \(g(\rho)\) is expressed in terms of another function \(h(\rho)\) defined as,

\[
h(\rho) = \sqrt{1 + (\kappa_D D/2\pi \rho)^2} + \frac{\varepsilon_w}{\varepsilon_c} \\
+ \left( \frac{\varepsilon_w}{\varepsilon_c} \sqrt{1 + (\kappa_D D/2\pi \rho)^2} + \frac{\varepsilon_c}{\varepsilon_w} \right) \\
\times \tanh (2\pi \rho d/D).
\]

Appendix B: Calculation of \(G(\xi)\) for \(\xi \ll 1\)

The function \(G(\xi)\) can be evaluated in the limit of small \(\xi\), given that it is expressed as

\[
G(\xi) = \frac{g(0,0)}{4} \xi^2 + \xi \sum_{n=1}^{\infty} g(n,0) \xi \\
+ \sum_{n,m=1}^{\infty} g(n, m) \xi^2.
\]

(B1)

Here, \(g(x, y)\) is a general well-behaved function of two variables. If \(\xi \to 0\), both the single and double sums have the form of a Riemann sum. To zero-th order in \(\xi\), they are equal to the one- and two-dimensional improper integrals over \(g(x, 0)\) and \(g(x, y)\), respectively.

However, in order to evaluate the derivative, \(G'(\xi)\), the zero-th order in \(\xi\) of these sums is not sufficient, and we use the Euler-Maclaurin formula [38],

\[
\sum_{n=1}^{\infty} g(n,0) \xi = \sum_{k=0}^{\infty} \frac{B_k}{k!} \xi^k \int_0^\infty \frac{\partial^k g}{\partial x^k} \bigg|_{y=0} dx, \quad (B2)
\]

where \(B_k\) are the Bernoulli numbers, with the first five given by

\[
B_0 = 1, B_1 = \frac{1}{2}, B_2 = \frac{1}{6}, B_3 = 0, B_4 = -\frac{1}{30}.
\]

If \(\lim_{x \to \infty} \frac{\partial^k g}{\partial x^k} = 0\) for all \(k\), Eq. (B2) implies that the expansion of \(\sum_{n=1}^{\infty} g(n,0) \xi\) in powers of \(\xi\) is

\[
\sum_{n=1}^{\infty} g(n,0) \xi = \int_0^\infty g(x,0) dx - \frac{g(0,0)}{2} \xi \\
- \frac{g'(0,0)}{12} \xi^2 + ...
\]

(B3)

For the double sum, the generalization of the Euler-Maclaurin formula is given by

\[
\sum_{n,m=1}^{\infty} g(n, m) \xi^2 = \sum_{j,k=0}^{\infty} \frac{B_j B_k}{j! k!} \xi^{j+k} \\
\times \int_0^\infty \int_0^\infty \frac{\partial^j g}{\partial x^j} \frac{\partial^k g}{\partial y^k} dxdy,
\]

(B4)

If \(g(x, y)\) has a radial symmetry, it can be written as \(g(x, y) = g(\rho)\) where \(\rho = \sqrt{x^2 + y^2}\), coinciding with the expression of \(g\) in Eq. (A4), where \(\rho = \xi\). We can then calculate the double integral in polar coordinates \((\theta, \rho)\), while recalling that \(g\) and all of its \(\rho\)-derivatives should vanish at infinity. These assumptions lead to the following expansion for the double sum,

\[
\sum_{n,m=1}^{\infty} g(n, m) \xi^2 = \int_0^{\pi/2} d\theta \int_0^\infty g(\rho) \rho d\rho \\
- \xi \int_0^\infty g(\rho) \rho d\rho + \frac{g(0)}{4} \xi^2 \\
+ \frac{g'(0)}{36} \xi^3 + ...
\]

(B5)

Finally, substituting Eqs. (B3) and (B5) into Eq. (B1), we obtain the expansion of \(G(\xi)\), for vanishing \(\xi\), as is used in Section IV.B,

\[
G(\xi) = \int_0^{\pi/2} d\theta \int_0^\infty g(\rho) \rho d\rho \\
- \frac{g'(0)}{18} \xi^3 + O(\xi^5).
\]

(B6)

Appendix C: Surface pressure and dipole interactions for \(\xi \ll 1\)

We present another way to obtain Eqs. (31)-(32). We start by considering the interaction energy between two parallel point-like dipoles of magnitude \(p\) at a large separation \(L\) that is perpendicular to the dipole direction. The dipoles are placed in the upper half-space having the permittivity \(\varepsilon_a\). Assuming that there is no contribution from the lower half-space (with permittivity \(\varepsilon_w \gg \varepsilon_a\)), the dipole-dipole interaction energy is [32]

\[
u_{\text{int}} = \frac{\tilde{p}^2}{8\pi \varepsilon_a \varepsilon_0 L^3}, \quad (C1)
\]

and is equal to one half of the familiar expression for interacting parallel dipoles. Summing over all pairs of parallel dipoles placed on a 2D lattice embedded in 3D space, the lattice cohesive energy, \(U_c\), is given by

\[
U_c = \frac{N}{2} \sum_{\rho_{nm} \neq 0} u_{\text{int}}(\rho_{nm}) \\
\approx 0.18N^{5/2} \frac{p^2}{\varepsilon_a \varepsilon_c A^{3/2}}, \quad (C2)
\]

\(A\) and \(B\) stand for the (1,1) and (1,2) modes, respectively.
where $\rho_{nm} = L(n, m)$ is an in-plane lattice vector, $N$ the number of particles (and lattice sites), and $A = NL^2$ the total surface area. Similar to the derivation of Eq. (3), we neglect the entropy of the large colloidal particles. Moreover, the entropy of the mobile electrolyte ions approaches the bulk-solution value, which is independent of the area, yielding $U_c = F_0 + \text{const}$.  

In Eq. (22), we performed a summation over all lattice sites,  
\[ \sum_{(m,n) \neq (0,0)} \frac{1}{(m^2 + n^2)^{3/2}} \approx 9.03. \]

The surface pressure is then recovered by taking $\Pi = -dF_0/dA \approx -dU_c/dA$,  
\[ \Pi \approx 0.269 \frac{p^2}{\varepsilon_0 \varepsilon R T}, \quad \text{(C3)} \]

Comparing Eq. (C3) with Eq. (31), we find the $p$ value as calculated above is $p = 0.99p_{\text{eff}}$ of the $p_{\text{eff}}$ in Eq. (31). Hence, in the dilute limit, Eq. (22) can be regarded as the effective dipole moment of the colloidal particle.


