Effective charges and virial pressure of concentrated macroion solutions

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The stability of colloidal suspensions is crucial in a wide variety of processes, including the fabrication of photonic materials and scaffolds for biological assemblies. The ionic strength of the electrolyte that suspends charged colloids is widely used to control the physical properties of colloidal suspensions. The extensively used two-body Derjaguin–Landau–Verwey–Overbeek (DLVO) approach allows for a quantitative analysis of the effective electrostatic forces between colloidal particles. DLVO relates the ionic double layers, which enclose the particles, to their effective electrostatic repulsion. Nevertheless, the double layer is distorted at high macroion volume fractions. Therefore, DLVO cannot describe the many-body effects that arise in concentrated suspensions. We show that this problem can be largely resolved by identifying effective point charges for the macroions using cell theory. This extrapolated point charge (EPC) method assigns effective point charges in a consistent way, taking into account the excluded volume of highly charged macroions at any concentration, and thereby naturally accounting for high volume fractions in both salt-free and added-salt conditions. We provide an analytical expression for the effective pair potential and validate the EPC method by comparing molecular dynamics simulations of macroions and monovalent microparticles that interact via Coulomb potentials to simulations of macroions interacting via the derived EPC effective potential. The simulations reproduce the macroion–macroion spatial correlation and the virial pressure obtained with the EPC model. Our findings provide a route to relate the physical properties such as pressure in systems of screened Coulomb particles to experimental measurements.

Coulomb interactions between ionized species affect colloidal suspensions at the microscopic level and have an indirect, yet crucial, impact on the observable macroscopic characteristics of the system (1). The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (2,3), proposed in the 1940s, has been crucial for understanding like-charged colloidal dispersions in a wide variety of experimental conditions. In this theory, the effective pair potential between two equally charged macroions immersed in an electrolyte is expressed as the sum of three terms: a hard-core potential that takes into account the excluded volume of macroions (preventing their overlap), an attractive potential due to short-range (van der Waals) interactions, and an electrostatic screened Coulomb or Yukawa potential resulting from the linearized Poisson–Boltzmann theory, which is the Debye–Hückel approximation. Many additions and modifications to the original theory have been proposed, including polarization effects, patchiness, or charge regulation, just to mention a few. Special care should be taken for nonaqueous solvents, divalent ions, or high salt concentrations, since, in these regimes, ion correlations are usually important (4–16). Generally speaking, modifications to the DLVO theory have been pivotal for systems in which many-body effects are crucial. This will allow previously improbable, mesoscale studies of colloidal assembly to be performed analytically or by simulation with implicit ions models.

Significance

Colloids constitute the basic components of many everyday products and are integrated into the fabric of modern society. Understanding their assembly is key for nanotechnological and biotechnological advances. At the single-particle level, colloids commonly possess electric charge. Consequently, the structure to which they conform is strongly influenced by electrostatic interactions. In solution, these interactions are modified by the presence of ions. We have developed a model for computing the corresponding effective electrostatic interactions as well as the osmotic pressure. Our model extends the applicability of Derjaguin–Landau–Verwey–Overbeek theory to dense systems in which many-body effects are crucial. This will allow previously impossible, mesoscale studies of colloidal assembly to be performed analytically or by simulation with implicit ions models.

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crystalline phase. This is also true of methods comprising the repulsive forces among macroions via hard-sphere interactions with effective hard-sphere radii (28–31). Different approaches such as the (renormalized) Jellium model (32) and methods that calculate the osmotic pressure within a Wigner–Seitz cell (33, 34) have been proposed. However, they do not yield information on the spatial configuration of the macroions and consequently are limited in describing dense macroion systems.

Model

In this work, we introduce a method to calculate the effective electrostatic pair interaction between macroions in dense systems through the identification of their corresponding effective point charges. We verify the corresponding accuracy by comparing the resulting radial distribution functions and pressures to the primitive model (PM). To begin, we consider spherical and impenetrable macroions of valency Z and radius a immersed in a 1:1 electrolyte with bulk concentration c. Traditionally for dilute macroion systems, the nonlinear PB theory establishes that the electrostatic potential is described by \(V = V(\Phi) = \lambda_r \sinh \Phi / (\kappa_B T)\), where \(\Phi\) is the electrostatic potential, \(\epsilon\) is the elementary charge, and \(k_B T\) is the thermal energy of the solution. The parameter \(\kappa_{\text{res}} = \sqrt{8\pi a \epsilon c}\) is an inverse screening length depending on the Bjerrum length interaction potentials (36, 37). Alexander et al. (33), however, can be embodied in an effective linear screening model by calculating the resulting radial distribution functions and pressures to point charges. We verify the corresponding accuracy by comparing the resulting radial distribution functions and pressures to the primitive model (PM). To begin, we consider spherical and radius \(a\).

For sufficiently small charges, the PB equation can be linearized by using sinusoidal screening potential, \(V = \Phi \approx \Phi_0\), resulting in the Debye–Hückel approximation, \(V = V(\Phi) = \kappa_{\text{res}} \sinh \Phi / (\kappa_B T)

The electrostatic potential outside the macroion, where \(\Phi = \Phi_0\), is the same as that of a point charge. Thus, the macroion is found to be \(\Phi = \Phi_0\), and the electrostatic force it exerts on a test charge (35), is the same as that of a point charge and is given by:

$$F = e \kappa_{\text{res}} \sinh \Phi / (\kappa_B T).$$

Apart from being restricted to dilute systems, the DLVO equation above cannot directly be applied to strongly charged macroions, since the Debye–Hückel approximation no longer holds for these systems, which, strictly speaking, leads to nonpairwise additive interaction potentials (36, 37). Alexander et al. (33), however, showed that nonlinear ion behavior close to the macroion surface can be embodied in an effective linear screening model by calculating a renormalized surface charge \(Z^*\) that, far away from the charged macroion surface, induces the same electrostatic potential and electric field as would be obtained within the nonlinear PB equation (33, 38–42); see Fig. 1F. Regarding a system of macroions at a concentration \(n_m\) and macroion packing fraction \(\eta \equiv 4\pi n_m a^3 / 3\), each of the macroions is imagined to be in the center of a charge-neutral spherical cell with radius \(R = a / \eta^{1/3}\), such that the summed volume of all cells matches the system’s volume (21). This is illustrated in Fig. 1C. In this spherical geometry, the nonlinear PB equation and the associated boundary conditions can be written as:

$$\Phi'(r) + \frac{2\Phi'(r)}{r} = \kappa_{\text{res}} \sinh \Phi(r)$$

where the prime denotes a derivative with respect to \(r\). The boundary conditions follow from Gauss’ law and include the global electroneutrality condition of the whole system. This set of equations is typically solved numerically, as no general analytical solution is known. Once the numerical solution is determined, one can therefore identify the effective model (Z) from the PM (Z) of monovalent microions and macroions of valency Z to the effective model (Z) where interactions are hard-core Yukawa with effective point charges \(Q\) (Fig. 1D) and PB calculations for the electric field (or charge within radius \(r\)) around a macroion following from nonlinear calculations (full line) and the Debye–Hückel fit (dashed line); \(I\) illustrates how surface charge renormalization yields a charge \(Z^*\) that can be inserted into DLVO theory. In the EPC approach, the effective point charge \(Q\) is calculated directly from the extrapolation displayed in \(G\).

$$\Phi(r) = Z^* \lambda_B / a^2 + e^{\kappa_{\text{res}} \sinh \Phi(r)} / (1 + \kappa_{\text{res}} a).$$

The accuracy and simplicity of the previous cell model approach can, however, be improved by calculating an effective point charge \(Q\) directly through identification of a point charge at \(r = 0\) by extrapolating the analytical approximation (see Fig. 1G), yielding the form \(Q \equiv \lim_{r \to 0} \Phi(r) r^2 / \lambda_B = (a_+ + a_-) / \lambda_B\). The latter can also be expressed as:

$$Q = \frac{\kappa_{\text{res}} \sinh \Phi_0}{\kappa_B T} \left[ e^{|R| \kappa_{\text{res}} \sinh \Phi_0 / \kappa_B T} - 1 \right].$$

The parameters \(\kappa\) and \(Q\) can then be used to approximate the effective electrostatic interactions in the original macroion system by those of point charges, using Eq. 1 to find the pairwise interaction energy. Although high macroion volume fractions...

Fig. 1. The various paths (\(B–D\)) from the PM (\(A\)) of monovalent microions and macroions of valency Z to the effective model (\(E\)) where interactions are hard-core Yukawa with effective point charges \(Q\); (\(F\) and \(G\)) PB cell calculations for the electric field (or charge within radius \(r\)) around a macroion following from nonlinear calculations (full line) and the Debye–Hückel fit (dashed line); \(I\) illustrates how surface charge renormalization yields a charge \(Z^*\) that can be inserted into DLVO theory. In the EPC approach, the effective point charge \(Q\) is calculated directly from the extrapolation displayed in \(G\).
render DLVO-based approaches inaccurate (21–25), the effective system of point charges has no hard-core volumes that will overlap with ionic double layers. We therefore expect that Eq. 3 in combination with Eq. 1 will remain accurate even in dense macroion systems. Note that the hard-core repulsions for $D < 2a$ should be maintained for the nonelectrostatic part of the pair interactions. Hereafter, we refer to the latter approach as the extrapolated point charge (EPC) method. The theoretical motivation for this approach is that screened Coulomb or Yukawa potentials solve the screened Poisson equation without considering the hard-core contribution of macroions at finite concentration. Thus, the main advantage of the EPC method is that it defines effective point charges in a consistent way, taking into account the excluded volume of highly charged macroions at any concentration.

In the regime where $Z$ is small and the resulting potential profile is sufficiently flat throughout the cell, $[\Phi(R) - \Phi(a)] \ll 1$, the analytical approximations to Eq. 3 will become exact on the entire space between the cell boundary and the macroion surface. As a consequence, $a_z$ can be calculated from $\Phi(a) = -Z\lambda_B/a^2$ and $\Phi(R) = 0$, and a direct analytical relation between $Z$ and $Q$ follows (Fig. 1D). Tantalizingly, inserting this $Q$ into Eq. 1 yields a pair potential similar to the DLVO equation,

$$\frac{U(D)}{k_BT} = \frac{Z^2\lambda_B e^{-\kappa Z}}{D[(1+\kappa a)(xR-1) + (1-\kappa a)(xR+1) e^{-2\kappa(xR-a)^2}]}$$

for $D \geq 2a$, and $V(D) = \infty$ for $D < 2a$. The screening parameter $\kappa$ that enters Eq. 4 reduces to the reservoir value $\kappa_{\text{urc}}$ for systems with a sufficient amount of added salt, for which $|\Phi_0| \ll 1$. Recall that $R = a_0 \eta^{-1/3}$ and that classical ($\eta$-independent) DLVO theory is reobtained for dilute suspensions, which is the limit of large $\eta$. For completeness, we confirm that in the limit of large double-layer size, $\kappa \gg D$, Eq. 4 reduces to the Coulombic form

$$\frac{U(D)}{k_BT} = \frac{Z^2\lambda_B}{D[(1-\eta)^2 + \frac{Z}{2\lambda_B}]}$$

for a macroion/microion mixture with particle diameters $d_M = 2a = 750$ Å and $d_s = d = 3$ Å, respectively, were performed in the constant number, volume, and temperature (NVT) ensemble using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package (47). This extreme size asymmetry between macroions and microions is selected to mimic realistic experimental colloidal systems. Macroions and monovalent microions, fulfilling the electroneutral condition, were placed inside a cubic simulation box of length $L$ under periodic boundary conditions.

In the PM representation that we applied here, ionic species are represented by repulsive-core spheres with point charges in their centers immersed in a continuous solvent (48–51). The pairwise forces among all particles have a short-range repulsive-core potential component, $u_{ij}^\text{urc}(D)$, and a long-range Coulombic pair potential contribution, $u_{ij}^\text{C}(D)/k_BT = \lambda_B^2Zz_i/z_j/D$, where $z_i$ and $z_j$ are the valences associated to particles $i$ and $j$, respectively. These interactions are handled properly, using the particle mesh Ewald technique (52). We model the repulsive-core pair potential between a particle of species $i$ and a particle of species $j$, separated by a distance $D$, as an impenetrable hard-core $u_{ij}^\text{urc}(D) = \infty$ for $D \leq \Delta_0$, a shifted–truncated Lennard–Jones potential $u_{ij}^\text{LJ}(D)/k_BT = 4(\sigma/D - \Delta_0)^{12} - (\sigma/D - \Delta_0)^{6} + 1$ for $\Delta_0 < D < \Delta_0 + 2^{1/6}\sigma$, and by a potential $u_{ij}^\text{C}(D) = 0$ for $D \geq \Delta_0 + 2^{1/6}\sigma$, where $\Delta_0 = (d_i + d_j)/2 - \sigma$ is the hard-core diameter. The parameter $\sigma$ regulates the hardness of the repulsive-core interactions. To mimic the hard-core interaction characteristic of the PM, $\sigma$ is set equal to 0.1 nm. We use $\lambda_B = 7.143$ Å throughout the text for theoretical and simulation calculations. Additional details of the simulation setup can be found in refs. 49–51.

**Results**

In Fig. 2, we compare radial distributions from computationally expensive PM MD simulations (circles) to much faster and more economic effective-model descriptions using MD simulations (solid lines), and integral equations (Fig. 2B, dashed lines). In the PM approach, we use a cubic simulation box of length $L = 8\lambda_B = 6,000$ Å, containing 360 macroions of valence $Z = 80$, 31,680 small monovalent counterions ($-\epsilon$), and 2,880 small

**Fig. 2.** Comparison of the pair correlation between macroions resulting from the full-ion PM MD simulations (circles) with those obtained by using repulsive-core effective screened Coulomb models (lines), relying on the the EPC approach (green) and surface charge renormalization approach (black). The solid lines in A represent MD simulations results, whereas the dashed lines in B were obtained from the Ornstein–Zernike equation within the RY closure; both A and B correspond to the same system in which the valence and packing fraction of the macroions in the PM are $Z = 80$ and $\eta = 0.3682$, respectively.

To verify our proposed prescription, molecular dynamic (MD) simulations of macroion/microion mixtures with particle diameters $d_M = 2a = 750$ Å and $d_s = d = 3$ Å, respectively, were performed in the constant number, volume, and temperature (NVT) ensemble using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package (47). This extreme size asymmetry between macroions and microions is selected to mimic realistic experimental colloidal systems. Macroions and monovalent microions, fulfilling the electroneutral condition, were placed inside a cubic simulation box of length $L$ under periodic boundary conditions.

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monovalent coions (+e). In the effective-model approach, microparticles are included implicitly in the Yukawa interactions between macroions with an effective charge \( Q \) and inverse screening length \( \kappa \).

The charges associated to the macroion profiles shown in Fig. 2 are \( \kappa = 204 \) following the EPC approach and \( \kappa = 167 \) following the surface charge renormalization approach in combination with the DLVO theory. An excellent agreement between the heavy-duty PM results, in which microions are included explicitly, and the computationally inexpensive MD Yukawa simulations using the EPC prescription can be observed in Fig. 2A. In contrast, surface charge renormalization in combination with the DLVO theory deviates significantly from PM simulation results, as expected at this volume fraction. The use of integral equations theory allows for an even faster numerical calculation of the radial distribution functions within the effective model. The Rogers–Young (RY) closure (53), which is known for its superb accuracy for hard-core Yukawa systems (46, 54–56), has good qualitative agreement compared with PM results, as seen in Fig. 2B. Note that PB techniques are grand canonical and therefore require a reservoir ion density \( n_{\text{res}} \) of counterions and coions, which is fixed, as there is no particle exchange with a reservoir. Therefore, we add an additional step to our PB method to obtain canonical results: for any choice of \( n_{\text{res}} \), we integrate the resulting ion profiles in the cell, which yields the total number of ions per macroion. The latter can be compared with the number of ions per macroion in the simulation box. Subsequently, the right value for \( n_{\text{res}} \) is determined by a root-finding procedure with respect to their difference.

The total microion/macroion pressure resulting from the PM, \( p_{\text{PM}} \), as well as the macroion pressure in the effective model, \( p_{\text{EM}} \), can be calculated via the virial equation \( p = (N/V)k_B T + (1/3V)(\sum_{i<j} D_{ij} U_{ij}(D_{ij})) \), where \( N \) sums all particles, in the PM, or only the macroions, in the effective model, and \( U_{ij}(D_{ij}) \) is the derivative with respect to the distance \( D_{ij} \) of the (un)screened Coulomb pair interaction between particles \( i \) and \( j \). However, to relate \( p_{\text{EM}} \) to \( p_{\text{PM}} \), it is essential to include a correction term that can be regarded as the pressure of a homogeneous background of counterions and coions, \( p_{\text{PM}} \approx p_{\text{EM}} + k_B T \frac{\kappa^2}{\pi \lambda_B} \left( 1 + \frac{4}{3} \frac{N_{\text{res}}}{N} \right) \).

Density functional theory (21, 22, 25, 57) may be applied for a rigorous derivation of this pressure difference, which shows up as EPC results, as well as the effective-model approximations following this approach is mainly applicable to systems with monovalent microparticles for which ion correlations are unimportant, although approximate extensions to systems with correlated multivalent counterions might be obtainable. We also propose a route to relate the pressure in the effective system of macroions to the osmotic pressure that can be measured experimentally in colloidal systems, for example, in sedimentation profiles (64, 65). Our method demonstrates accuracy with respect to acquiring the measurable properties of charged colloidal suspensions, and can therefore be applied to guide and interpret experiments on related systems.

**Conclusions**

In this work, we have introduced a method that extends the capabilities of the DLVO theory to high valences and volume fractions of colloidal macroions using no additional assumptions besides the underlying PB theory. Akin to the original theory, this approach is mainly applicable to systems with monovalent microparticles for which ion correlations are unimportant, although approximate extensions to systems with correlated multivalent counterions might be obtainable. We also propose a route to relate the pressure in the effective system of macroions to the osmotic pressure that can be measured experimentally in colloidal systems, for example, in sedimentation profiles (64, 65). Our method demonstrates accuracy with respect to acquiring the measurable properties of charged colloidal suspensions, and can therefore be applied to guide and interpret experiments on related systems.

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