Colloidal particles, typically nanometers to microns in size, commonly acquire electric charge in solution \[1\]. Practical examples are latex microspheres in paints, ionic micelles in detergents, and platelets in clay suspensions. Beyond traditional applications, e.g., in the chemical, pharmaceutical, and mining industries, the rich thermal and optical properties of charged colloidal crystals have inspired recent proposals for novel technologies, such as fast optical switches and photonic band-gap materials \[2\].

Among the various interparticle interactions at play in charged colloids, electrostatic interactions strongly affect thermodynamic stability and materials properties \[3\]. The classic theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) \[4\] describes the bare Coulomb interaction for the electrostatic potential around a macroion \[4\].

Density-functional \[6\] and linear response \[8, 9\] theories offer alternative routes to effective interactions, but also yield, as an important by-product, a one-body (volume) energy. Numerical results demonstrate that nonlinear effects can substantially modify effective interactions and thermodynamics of aqueous, low-salt suspensions of highly-charged macroions.

The DLVO pair potential was originally derived by linearizing the mean-field Poisson-Boltzmann (PB) equation for the electrostatic potential around a macroion \[4\]. As the interaction for \( r < \sigma/2 \) is arbitrary, \( \alpha \) is chosen to minimize counterion penetration inside the core \[7\].

The mixture of macroions and counterions is formally reduced to an equivalent one-component system of “pseudo-macroions” by performing a restricted trace over counterion coordinates, keeping the macroions fixed. Denoting counterion and macroion traces by \( \langle \rangle_c \) and \( \langle \rangle_m \), respectively, the canonical partition function is

\[
Z = \langle \exp(-\beta H) \rangle_{c,m} = \langle \exp(-\beta H_{eff}) \rangle_m ,
\]

where \( H_{eff} = H_m + H_c \) is the effective one-component Hamiltonian, \( \beta = 1/k_BT \), and

\[
F_c = -k_BT \ln \langle \exp[-\beta(H_c + H_{mc})] \rangle_c
\]

is the free energy of a nonuniform gas of counterions in the presence of the macroions. Adding to \( H_c \) (and subtracting from \( H_{mc} \)) the energy of a uniform compensating negative background, \( E_b \), converts \( H_c \) to the Hamiltonian

Nonlinear Screening and Effective Interactions in Charged Colloids

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Influences of nonlinear screening on effective interactions between spherical macroions in charged colloids are described via response theory. Nonlinear screening, in addition to generating effective many-body interactions, is shown to entail essential corrections to the pair potential and one-body volume energy. Numerical results demonstrate that nonlinear effects can substantially modify effective interactions and thermodynamics of aqueous, low-salt suspensions of highly-charged macroions.

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of a classical one-component plasma (OCP) of counterions. In practice, the OCP is weakly correlated, with coupling parameter \( \Gamma = \lambda_B/\alpha_c \ll 1 \), where \( \lambda_B = \beta k^2/\epsilon \) is the Bjerrum length and \( \alpha_c = (3/4\pi n_c)^{1/3} \). The OCP has mean density \( n_c = N_c/V(1-\eta) \), since the counterions are excluded (with the background) from the macroion core volume fraction, \( \eta = \frac{6}{\pi}(N_m/V)^{3/4} \).

The counterion free energy is approximated by regarding the macroions as “external” potential for the OCP and invoking perturbation theory \([8, 10]\):

\[
F_c = F_{OCP} + \int_0^1 d\lambda \langle H_{mc}^\lambda \rangle, \tag{4}
\]

where \( F_{OCP} = -k_B T \ln \langle \exp[-\beta (H_c + E_b)] \rangle \) is the OCP free energy, \( H_{mc} = H_{mc} - E_b \), and the \( \lambda \)-integral charges the macroions. In terms of Fourier components,

\[
\langle H_{mc}^\lambda \rangle = \frac{1}{V} \sum_k \hat{v}_{mc}(k) \hat{\rho}_m(k) \langle \hat{\rho}_c(-k) \rangle, \tag{5}
\]

where \( \hat{v}_{mc}(k) \) is the Fourier transform of Eq. \( [1] \) and \( \hat{\rho}_m(k) \) and \( \hat{\rho}_c(k) \) are Fourier components of the macroion and counterion number densities. Now, to second order in the macroion density, we may write (for \( k \neq 0 \))

\[
\hat{\rho}_c(k) = \chi^{(1)}(k) \hat{v}_{mc}(k) \hat{\rho}_m(k) + \frac{1}{V} \sum_{k'} \chi^{(2)}(k', k - k') \hat{v}_{mc}(k') \hat{\rho}_m(k') \hat{\rho}_m(k) \tag{6}
\]

where \( \chi^{(1)} \) and \( \chi^{(2)} \) are, respectively, the linear and first nonlinear response functions of the OCP \([11]\).

To specify the response functions, we adopt the random phase approximation (RPA), which equates the two-particle direct correlation function of the OCP to its exact asymptotic limit: \( \chi^{(2)}(r) = -\beta v_{cc}(r) \). Within the RPA, \( \chi^{(1)} \) and \( \chi^{(2)} \) have analytic forms

\[
\chi^{(1)}(k) = \frac{-\beta n_c}{1 + k^2/k^2}, \tag{7}
\]

where \( \kappa = \sqrt{4\pi n_c^2 \lambda_B} \), and

\[
\chi^{(2)} = \frac{-\beta^2 n_c^2/2}{(1 + k^2/k^2)(1 + k^2/k^2)(1 + k^2/k^2)(1 + k^2/k^2)}. \tag{8}
\]

With the response functions specified, the counterion density can be explicitly determined from Eq. \( [1] \). Penetration inside the macroion cores is reduced, to at most a few per cent, by choosing \( \alpha = \kappa \sigma/(2+\kappa \sigma) \) in Eq. \( [1] \). Salt is incorporated via additional response functions for the multiple microion species. In the process, \( \kappa \) is modified by replacing the counterion density, \( n_c \), by the total microion density, \( n_\mu = n_+ + n_- \), where \( n_\pm = N_\pm/V(1-\eta) \) are the densities of positive and negative microions.

Combining Eqs. \( [4] \), \( [5] \), the effective Hamiltonian can be written as a sum of one-, two-, and three-body terms. The one-body term, or volume energy, is the sum of

\[
E_0 = F_{OCP} - \frac{k_B T N_m}{2} \left( \frac{Z^2 \lambda_B \kappa}{1 + \kappa \sigma/2} - \frac{Z n_c}{n_\mu} \right), \tag{9}
\]

which is the linear response volume energy \([1] \), and

\[
\Delta E = k_B T \frac{N_m n_c}{6 n_\mu^2} \int dr \left( \frac{[\rho_0(r)]^2 - \frac{1}{n_\mu}[\rho_0(r)]^3}{\rho_0(r)} \right) \tag{10}
\]

which is the first nonlinear correction, with

\[
\rho_0(r) = \frac{Z^2}{Z^2} \frac{\kappa^2}{4\pi} \left( \frac{e^{\kappa \sigma/2}}{1 + \kappa \sigma/2} \right) e^{-\kappa \sigma}, \quad r > \sigma/2 \tag{11}
\]

being the linear response counterion density orbital around a single macroion. In Eq. \( [10] \), \( \kappa \) can be identified now as an inverse Debye screening length. The first and second terms on the right side of Eq. \( [10] \) account, respectively, for the counterion entropy and the macroion-counterion electrostatic interaction energy, while Eq. \( [10] \) corrects the latter term for nonlinear screening.

The two- and three-body terms in \( H_{eff} \) involve effective pair and triplet interactions. The pair interaction, \( \nu_0^{(2)}(r) \), is the sum of the linear response form \([1]\)

\[
\nu_0^{(2)}(r) = \frac{Z^2 e^2}{\epsilon} \left( \frac{e^{\kappa \sigma/2}}{1 + \kappa \sigma/2} \right) \frac{e^{-\kappa \sigma}}{r}, \quad r > \sigma, \tag{12}
\]

i.e., the DLVO potential \([1] \) (aside from the excluded-volume adjustment to \( \kappa \)), and the nonlinear correction

\[
\Delta \nu^{(2)}(r) = -k_B T \frac{n_c}{n_\mu^2} \int dr' \rho_0(|r - r'|) \rho_0(r') \tag{13}
\]

\[
\times \frac{\rho_0(r') - \frac{n_\mu}{3}}{\rho_0(r' - \frac{n_\mu}{3})}. \tag{14}
\]

Finally, the triplet interaction is

\[
\nu^{(3)}(r_1, r_2, r_3) = -k_B T \frac{n_c}{n_\mu^2} \int dr \rho_0(|r_1 - r|) \tag{15}
\]

\[
\times \rho_0(|r_2 - r|) \rho_0(|r_3 - r|). \tag{16}
\]

Note that, with increasing salt concentration or decreasing macroion volume fraction \( n_c/n_\mu \rightarrow 0 \), the nonlinear corrections, \( \Delta E \) and \( \Delta \nu^{(2)}(r) \), and the effective triplet interaction, all diminish in relative magnitudes. Thus, nonlinear effects are strongest for deionized suspensions.

Equations \( [11] \), \( [12] \), and \( [13] \) are the main theoretical results of the paper. Equation \( [12] \), which is a bulk nonlinear correction to \( \nu_0^{(2)}(r) \), is similar in structure to a wall-induced pair interaction derived in Ref. \( [12] \) [Eq. (13) therein]. Furthermore, Eq. \( [13] \) is consistent with the triplet force derived in Ref. \( [13] \) [Eq. (33) therein]. The response theory, in neglecting short-range correlations between microions, is formally equivalent to the mean-field PB theory. Its scope is therefore limited to long-range interactions between macroions. However, whereas numerical solutions of the nonlinear PB equation are practical only within symmetric Wigner-Seitz cells, characteristic of crystals (PB cell models) \([1, 4]\), the effective interactions derived here apply, in principle, to any bulk phase.
We can now quantify the practical significance of nonlinear screening by evaluating the effective pair interaction and volume energy for selected system parameters. All results presented are for bulk, aqueous suspensions ($\lambda_B = 0.714$ nm) and monovalent counterions ($z = 1$). Analytic reduction of Eqs. (10) and (13) was checked by Monte Carlo integration. Figure 1 shows the effective pair potential for macroions of diameter $\sigma = 100$ nm, valence $Z = 700$, and volume fraction $\eta = 0.01$ at ionic strength $c_s = 1$ $\mu$M. The chosen charge is comparable to the maximum renormalized charge (allowing for counterion condensation), $Z^* = C\sigma/\lambda_B$, where $C = O(10)$ [14]. At short and intermediate ranges, nonlinear screening sharpens the counterion profile around a macroion, which, as seen in Fig. 1, weakens the pair repulsion. This result is consistent, if only qualitatively, with bulk measurements [15] of pair interactions shorter than predicted by DLVO theory. At longer range (inset), nonlinear screening changes the asymptotic form to $v^{(2)}(r) \sim e^{-\kappa r}$, a qualitative departure from the more rapidly decaying DLVO form, $v^{(2)}_0(r) \sim e^{-\kappa r}/r$. As the macroion charge increases, higher-order nonlinear effects ultimately manifest themselves. In fact, for values of $Z > Z^*$ the effective pair potential can actually become attractive. Since pair attractions are mathematically excluded within the PB theory [16], higher-order nonlinear terms must then also contribute in such extreme cases. Within physical parameter ranges ($Z < Z^*$), however, $v^{(2)}(r)$ is always repulsive. Interestingly, the short-to-intermediate-range part of the nonlinear pair potential may still be reasonably fit by a DLVO-like potential.

The cleanest test of the theory is comparison with 

**FIG. 1:** Effective pair interaction between macroions of diameter $\sigma = 100$ nm, valence $Z = 700$, and volume fraction $\eta = 0.01$ at ionic strength $c_s = 1$ $\mu$M. Solid curve: nonlinear screening. Dashed curve: linear screening (DLVO). Inset: cross-over from $e^{-\kappa r}/r$ to $e^{-\kappa r}$ behavior at longer range.

**FIG. 2:** Total interaction potential energy for two macroions of diameter $\sigma = 106$ nm and valence $Z = 200$, at zero ionic strength, in a cubic box of length $530$ nm with periodic boundary conditions. Solid curve: nonlinear screening prediction. Dashed curve: linear screening (DLVO) prediction. Symbols: *ab initio* simulation data [17].

...
nonlinear effects may thus facilitate any fluctuation-mediated short-range attractions \cite{7, 18} and help to explain anomalous phase behavior observed in experiments \cite{7, 18}, as well as in recent simulations \cite{20}.

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nnificantly affect phase stability of highly-charged, deionized suspensions. In fact, the parameter ranges in which instabilities toward phase separation have thus far been predicted \cite{7, 18} lie well within the nonlinear regime. Future work will further explore influences of nonlinearity, including the role of attractive triplet interactions, on thermodynamics of charged colloids.

In summary, applying response theory to the primitive model of charged colloids, we have consistently extended the DLVO linear-screening theory by including leading-order nonlinear contributions to effective interactions between macroions. A major conclusion is that nonlinear corrections, aside from generating effective many-body interactions, can significantly modify the effective pair interaction and volume energy, and thus thermodynamics, of deionized suspensions of highly charged macroions. While mean-field pair interactions are repulsive at long range, nonlinear screening weakens shorter-range pair repulsion and generates effective three-body attractions. Nonlinear effects may thus facilitate any fluctuation-mediated short-range attractions \cite{7} and help to explain anomalous phase behavior observed in experiments \cite{7, 18}, as well as in recent simulations \cite{20}.

FIG. 3: Nonlinear deviations from DLVO theory for macroion diameter $\sigma = 100$ nm and valences, from top to bottom, $Z = 500, 600, 700$. Systems with macroion volume fraction, $\eta$, and ionic strength, $c_s$, above the curve deviate from the DLVO pair potential by at least 20% at the fcc-crystal nearest-neighbor distance.

FIG. 4: Volume energy contribution, $P_v$, to the total reduced pressure vs. volume fraction, $\eta$, for macroion diameter $\sigma = 500$ nm and valence $Z = 4000$ at ionic strength $c_s = 1 \mu M$. Solid curve: nonlinear screening prediction. Dashed curve: linear screening (DLVO) prediction.

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