Effective electrostatic interactions in mixtures of charged colloids

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We present a theory of effective electrostatic interactions in polydisperse suspensions of charged macroions, generalizing to mixtures a theory previously developed for monodisperse suspensions. Combining linear response theory with a random phase approximation for microion correlations, we compute radial distribution functions of binary mixtures of oppositely charged colloidal macroions from molecular dynamics simulations of the coarse-grained model (with implicit microions), taking effective pair potentials as input. Our results agree closely with corresponding results from more computationally intensive Monte Carlo simulations of the primitive model (with explicit microions). Simulations of a mixture with large size and charge asymmetries indicate that charged nanoparticles can enhance electrostatic screening of charged colloids. The theory presented here lays a foundation for future large-scale modeling of complex mixtures of charged colloids, nanoparticles, and polyelectrolytes.

I. INTRODUCTION

Soft materials, such as suspensions of colloids or nanoparticles and solutions of polymers or surfactants, are complex mixtures of microscopic and mesoscopic components. Polydispersity in the intrinsic properties of macromolecules or mesoscopic particles can significantly modify intermolecular (interparticle) forces and in turn self-assembly and macroscopic behavior. While rigid particles have static distributions of size and shape, polymer coils in solution can fluctuate in conformation. Further variation can arise when counterions dissociate (in water or other polar solvents), leaving colloidal or polyelectrolyte macroions with a broad charge distribution.

The influence of polydispersity on thermodynamic phase behavior, structure, and dynamics of soft materials has drawn increasing attention in recent years. This trend stems not only from fundamental interest in the rich materials properties of mixtures, but also from the prevalence of polydispersity in natural colloids, such as clays and many biological systems. Moreover, tuning interparticle forces has practical applications in stabilizing unusual morphologies and engineering novel materials.

Thermal and structural properties of bidisperse colloidal mixtures have been explored by a variety of experimental methods, including light scattering and microscopy. Theoretical and computational studies have applied integral-equation methods, classical density-functional theory (DFT), and computer simulations. Recent related work has explored mixtures of colloids and nanoparticles, characterized by extreme asymmetries in size and charge, via experiments, integral-equation theory, and simulation.

In modeling charged colloids, electrostatic interactions between macroions are commonly approximated by Yukawa (screened-Coulomb) effective pair potentials, as first derived in the classic works of Derjaguin and Landau, and Verwey and Overbeek. The Debye-Hückel theory of electrolytes. Studies of charged colloidal mixtures also typically assume Yukawa pair potentials, which emerge from generalizing either the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory or integral-equation theories based on the mean spherical approximation. For salty suspensions, in which direct Coulomb interactions are strongly screened by microions (counterions and salt ions), the Yukawa model has proven reasonably accurate. Recent observations of deionized mixtures, however, have called into question the accuracy of the Yukawa model when applied to weakly-screened macroions.

Previously, one of us modeled effective electrostatic interactions in one-component (monodisperse) suspensions of charge-stabilized colloids and polyelectrolyte solutions using linear response theory. Within a mean-field (random-phase) approximation, equivalent to Poisson-Boltzmann theory in its neglect of correlations between microions, linear response theory recovers the usual Yukawa effective pair potential between nonoverlapping macroions, but with a screening constant that depends on both salt and macroion densities and consistently incorporates excluded volume. Beyond a density-dependent effective pair potential, the theory also predicts a one-body volume energy, as do related approaches to effective interactions based on integral-equation theories, classical density-functional theory, and computer simulations.
functional theory \[54\], and extended Debye-Hückel theories \[53, 55\]. Although independent of macroion coordinates, the volume energy contributes to the free energy a term that depends on macroion density and thus can affect bulk thermodynamic properties at low salt concentrations (approaching counterion concentrations).

The volume energy has been identified \[64, 58, 59\] as a possible origin of anomalous phase behavior observed in deionized monodisperse suspensions \[61, 70\]. Theoretical modeling is complicated, however, by nonlinear screening \[71\] and charge regulation \[22, 44, 72–74\]. In a recent extension of the DFT approach, Bier et al. \[30\] presented an expression for the volume energy of bidisperse charged colloids. A subsequent experimental study \[12\] invoked this volume energy as a possible explanation of unusual fluid-crystal phase separation in deionized binary mixtures with large charge asymmetry. Accurate theoretical predictions of the complex phase behavior of colloidal mixtures over a vast parameter space require a reliable theory of effective interactions.

In this paper we generalize linear response theory to polydisperse mixtures of macroions. In Sec. \[II\] we begin by defining the primitive model of charged colloids and polyelectrolytes. Within the primitive model, we develop in Sec. \[III\] the generalization of linear response theory to polydisperse mixtures and derive general expressions for the effective interactions. In Sec. \[IV\] we present explicit analytical expressions for the effective pair potentials and volume energies of polydisperse suspensions of charged hard-sphere colloids and compare with previous theoretical results. In Sec. \[V\] and the Appendix we discuss the calculation of structural and thermodynamic properties of bidisperse colloidal suspensions as functions of size and charge ratios. Finally, in Sec. \[VI\] we summarize and conclude with suggestions for future applications.

II. PRIMITIVE MODEL OF MIXTURES

We consider spherical macroions of various species \((m = 1, 2, 3, \ldots)\), having diameters \(\sigma_m\) (radii \(a_m\)) and valences \(Z_m\), suspended in a solvent with microions (species \(\mu = 1, 2, 3, \ldots\)) of valences \(z_\mu\) (see Fig. \[I\]). Adopting the primitive model of charged colloids and polyelectrolytes, we treat the solvent as a dielectric continuum of dielectric constant \(\varepsilon\) that reduces the strength of electrostatic interactions. The macroions are confined to a fixed volume \(V\), while the microions (counterions, salt ions) are free to exchange with an electrolyte reservoir (e.g., via a semipermeable membrane), which maintains a fixed salt chemical potential (Donnan equilibrium) at absolute temperature \(T\). For simplicity, we model the microions as point ions and assume a symmetric electrolyte of salt ion pairs with valences \(z_+\) and \(z_-\).

The Hamiltonian of this model system can be separated according to \(H = H_{\text{core}} + H_{\text{el}}\), where \(H_{\text{core}}\) incorporates interactions between macroion cores, as well as the total kinetic energy, and \(H_{\text{el}}\) is the total Coulomb electrostatic energy:

\[
H_{\text{el}} = H_m + H_\mu + H_{m\mu}.
\]

The first term on the right-hand side accounts for interactions among macroions \((m)\), the second term interactions among microions \((\mu)\), and the last term macroion-microion interactions. An explicit expression for the macroion Hamiltonian is

\[
H_m = \sum_m N_m \left( \sum_{i<j} N_{i<} v_{mn}(r_{ij}) + \sum_{m<n} N_m N_n v_{mn}(r_{ij}) \right),
\]

where \(N_m\) is the number of macroions of species \(m\) and \(v_{mn}(r_{ij}) = Z_m Z_n e^2/\varepsilon r_{ij}\) is the (Coulomb) potential energy between a pair of macroions (labeled \(i\) and \(j\)) of species \(m\) and \(n\) separated by center-to-center distance \(r_{ij}\), \(e\) being the electron charge. Similarly, the macroion Hamiltonian is

\[
H_\mu = \sum_\mu N_\mu \left( \sum_{i<j} N_{i<} v_{\mu\mu}(r_{ij}) + \sum_{\mu<\nu} N_\mu N_\nu v_{\mu\nu}(r_{ij}) \right),
\]

where \(N_\mu\) is the number of microions of species \(\mu\) and \(v_{\mu\nu}(r_{ij}) = z_\mu z_\nu e^2/\varepsilon r_{ij}\) is the potential energy between a pair of microions of species \(\mu\) and \(\nu\). Finally, the macroion-microion interaction Hamiltonian is given by

\[
H_{m\mu} = \sum_{m,\mu} \sum_{i=1}^{N_m} \sum_{j=1}^{N_\mu} v_{mn}(r_{ij}),
\]

where \(v_{mn}(r_{ij}) = Z_m Z_n e^2/\varepsilon r_{ij}\) is the macroion-microion pair potential energy. Latin and Greek subscripts here refer to macroions and microions, respectively. Note that the subscripts \(m\) and \(\mu\) are used both to represent macroions and microions as a whole and as an index to label different species of macroion and microion, the distinction being clear from the context. The condition of global electroneutrality dictates that \(\sum_m Z_m N_m + \sum_\mu z_\mu N_\mu = 0\).

III. LINEAR RESPONSE THEORY

Within the primitive model, we outline a general coarse-graining approach to modeling effective electrostatic interactions in polydisperse suspensions of charged macroions, extending to mixtures the linear response theory formulated previously for monodisperse suspensions of spherical macroions \[39, 40\]. Integrating out microion degrees of freedom from the partition function, assuming linear response of microion densities to macroion electrostatic potentials, and making a mean field approximation for the microion response functions, we obtain effective pair potential energies between macroion species \(m\) and \(n\) of the form

\[
v_{mn,\text{eff}}(r) = A_{mn} \exp(-kr) / r, \quad r > a_m + a_n.
\]
where $\kappa$ is the inverse Debye screening length and the prefactors $A_{mn}$ depend on macroion sizes and charges. Equation (6) is the well-known Yukawa effective pair potential assumed in many simulation studies \[11, 75, 76\]. In addition to confirming the general form of the effective pair potentials, however, our approach also incorporates macroion excluded volume into the screening constant and yields a one-body volume energy, which depends on the bulk densities of all microions (both salt ions and counterions).

### A. Coarse graining microion degrees of freedom

We begin by extending to mixtures a general statistical mechanical procedure for formally averaging over microion degrees of freedom such that the system partition function remains unchanged. If this averaging is performed exactly, the resulting coarse-grained model will reproduce thermodynamic properties of the original model \[43, 77\]. The canonical partition function for our model mixture is given by

$$Z = \langle \exp(-\beta H) \rangle_m, \quad (6)$$

where $\beta = 1/k_B T$ and the angular brackets represent classical traces over relevant degrees of freedom. After coarse graining, achieved by integrating over microion degrees of freedom for a fixed macroion configuration, Eq. (6) can be re-expressed as

$$Z = \langle \exp(-\beta H_{\text{eff}}) \rangle_m, \quad (7)$$

where $H_{\text{eff}} = H_{\text{core}} + H_m + F_\mu$ and

$$F_\mu \equiv -k_B T \ln \langle \exp[-\beta(H_\mu + H_{m\mu})] \rangle_\mu. \quad (8)$$

can be interpreted as the free energy of microions in a fixed configuration of macroions. To make coarse-grained models of effective interactions practical for simulations or further theoretical development, approximations are necessary to render $F_\mu$ in an analytical or numerically computable form.

### B. Linear response approximation for microions

Following the general approach of Silbert and co-workers \[78–80\], we regard the interactions of the macroions with the microions as external perturbations to a uniform microion plasma. As a first step, we define an intermediate free energy as a function of a charging parameter $\lambda$,

$$F_\mu(\lambda) \equiv -k_B T \ln \langle \exp[-\beta(H_\mu + \lambda H_{m\mu})] \rangle_\mu. \quad (9)$$

With this definition, $F_\mu = F_\mu(\lambda = 1)$ can be written as

$$F_\mu = F_\mu(0) + \int_0^1 d\lambda \langle H_{m\mu} \rangle_\lambda, \quad (10)$$

where $\langle \rangle_\lambda$ denotes an average over microion degrees of freedom in a system where the macroions are charged to a fraction $\lambda$ of their full charges.

In Eq. (10), $F_\mu(0)$ is the free energy of a reference system consisting of a classical gas of microions in a free volume $V_f = V(1 - \eta)$, which excludes the fraction

$$\eta = \frac{4\pi}{3V} \sum_m N_m a_m^3. \quad (11)$$

of the total volume that is occupied by macroion hard cores. To ensure that the reference system is electroneutral, it is convenient to add to and subtract from $F_\mu(0)$ the energy of a uniform compensating background charge distribution, occupying the same free volume, having uniform number density

$$p_b = \frac{1}{V_f} \sum_m Z_m N_m. \quad (12)$$

Denoting the energy of this background by

$$E_b = -\frac{V_f p_b^2}{2e} \lim_{k \to 0} \frac{4\pi e^2}{k^2}, \quad (13)$$

we can redefine the microion interaction energies as

$$H'_\mu \equiv H_\mu + E_b, \quad H'_{m\mu} \equiv H_{m\mu} - E_b. \quad (14)$$

The microion free energy $F_\mu$ then can be expressed as

$$F_\mu = F_p + \int_0^1 d\lambda \langle H'_{m\mu} \rangle_\lambda, \quad (15)$$

where $F_p = -k_B T \ln \langle \exp(-\beta H'_p) \rangle_\mu$ is the free energy of a microion plasma with the neutralizing background charge density $e p_b$. 

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FIG. 1. Primitive model of binary mixture of charged colloids: two species of charged macroion (valences $Z_1$ and $Z_2$), microions (counterions and salt ions), and implicit solvent.
The next step in approximating $F_\mu$ is to relate the macroion-microion Hamiltonian [Eq. (13)] to number density operators $\rho_m(r)$ and $\rho_\mu(r)$ of macroions and microions, respectively, and to the macroion-microion pair potentials $v_{m\mu}(r)$:

$$H_{m\mu} = \sum_m \sum_\mu \int_{V_f} dr \int_{V_f} dr' \rho_m(r)v_{m\mu}(|r - r'|)\rho_\mu(r') .$$

The integrand in Eq. (15) then can be expressed in terms of Fourier components:

$$\langle H'_{m\mu} \rangle_\lambda = \frac{1}{V_f} \sum_m \sum_\mu \sum_\mathbf{k} \hat{\rho}_m(\mathbf{k})\hat{v}_{m\mu}(\mathbf{k}) \langle \hat{\rho}_\mu(-\mathbf{k}) \rangle_\lambda - E_b ,$$

where the Fourier transforms are defined over the free volume, for example,

$$\hat{\rho}_m(\mathbf{k}) = \int_{V_f} dr \rho_m(r)\exp(-i\mathbf{k} \cdot \mathbf{r}) .$$

To develop a response theory, we first define an external potential applied by the macroions to the (otherwise uniform) microion plasma:

$$v_{\text{ext}}(r) \equiv \sum_m Z_m \int dr' v_m(|r - r'|)\rho_m(r') ,$$

where $v_m(r) \equiv v_{m\mu}(r)/Z_m z_\mu$. We then make the approximation that the microion densities respond linearly to the macroion external potential. Denoting by $\chi_{\mu\nu}(k)$ the linear response functions of the unperturbed microion plasma (with $\lambda = 0$), and defining $\chi_\mu(k) \equiv \sum_\nu z_\nu \chi_{\nu\mu}(k)$, then to linear order in the external potential

$$\langle \hat{\rho}_\mu(\mathbf{k}) \rangle_\lambda = \chi_\mu(k)\langle \hat{v}_{\text{ext}}(\mathbf{k}) \rangle, \quad k \neq 0 ,$$

the Fourier transform of the external potential being

$$\hat{v}_{\text{ext}}(\mathbf{k}) = \sum_m Z_m \hat{v}_m(\mathbf{k})\rho_m(\mathbf{k}) .$$

Note that the $k = 0$ component must be excluded since $\hat{\rho}_\mu(0) = N_\mu$ is fixed by the condition of electroneutrality.

Using Eqs. (17) and (20), the linear response approximation for the microion free energy [Eq. (15)] can be expressed as

$$F_\mu = F_p + \frac{1}{2V_f} \sum_m \sum_\mu \sum_\mathbf{k} \hat{\rho}_m(\mathbf{k})\hat{v}_{m\mu}(\mathbf{k}) \chi_\mu(k)\langle \hat{v}_{\text{ext}}(-\mathbf{k}) \rangle - \frac{1}{V_f} \sum_m N_m N_\mu \lim_{k \rightarrow 0} \hat{v}_{m\mu}(k) - E_b .$$

Equation (22) can be recast in the more intuitive form

$$F_\mu = \sum_m \sum_{i < j} N_{m,\text{ind}}(r_{ij}) + \sum_{m < n} \sum_{i = 1}^{N_m} \sum_{j = 1}^{N_n} N_{m,\text{ind}}(r_{ij}) + E_0 ,$$

where $v_{m,\text{ind}}(r)$ are microion-induced pair potentials between macroions, whose Fourier transforms are given by

$$\hat{v}_{m,\text{ind}}(k) = Z_m Z_n \hat{v}_m(k)\hat{v}_n(k) \sum_\mu z_\mu \chi_\mu(-k) ,$$

and $E_0$ is a one-body volume energy:

$$E_0 = F_p + \frac{1}{2} \sum_m N_m \lim_{r \rightarrow 0} v_{m,\text{ind}}(r) - \frac{1}{2V_f} \sum_m N_m N_\mu \lim_{k \rightarrow 0} \hat{v}_{m\mu}(k) + \frac{1}{V_f} \sum_m N_m N_\mu \lim_{k \rightarrow 0} \hat{v}_{m\mu}(k) - E_b .$$

Equation (25) suggests expressing the effective Hamiltonian as

$$H_{\text{eff}} = H_{\text{core}} + \sum_m \sum_{i < j} v_{m,\text{eff}}(r_{ij}) + \sum_{m < n} \sum_{i = 1}^{N_m} \sum_{j = 1}^{N_n} v_{m,\text{eff}}(r_{ij}) + E_0 ,$$

thus identifying

$$v_{m,\text{eff}}(r) = v_m(r) + v_{m,\text{ind}}(r)$$

as an effective (microion-mediated) pair potential between macroions of species $m$ and $n$.

Note that our coarse-grained model involves only one- and two-body effective interactions, which is a direct consequence of the linear approximation for the response of the microion densities [Eq. (20)]. Nonlinear response entails many-body effective interactions, as well as corrections to the one- and two-body interactions [71]. The linear response approximation is reasonable for sufficiently weakly charged macroions and proves valid even for highly charged macroions if the bare valence is replaced by an effective valence via charge renormalization theory [44, 73, 74]. For monodisperse suspensions, the theory accurately predicts thermodynamic and structural properties (osmotic pressures and radial distribution functions) for electrostatic coupling strengths as high as $Z_m \lambda_B/a_m \simeq 15$ [44, 73, 74].

**IV. ANALYTICAL RESULTS**

Calculating effective interactions in polydisperse mixtures of charged colloids requires approximating the linear response functions $\chi_\mu(k)$. Following previous studies of monodisperse charged colloids [39, 40], we adopt the random-phase approximation, which provides $\chi_\mu(k)$ in analytical form and thus yields analytical expressions for the induced pair potentials between macroions, from Eq. (24), and for the volume energy, from Eq. (25).
A. Response functions of the microion plasma

The linear response functions of the reference microion plasma are proportional to the corresponding partial structure factors [81]:

\[ \chi_{\mu\nu}(k) = -\beta \sum_{\mu} n_{\mu} S_{\mu\nu}(k), \]  

(28)

where \( n_{\mu} = N_{\mu}/V_f \) is the average number density of microion species \( \mu \) in the free volume, thus incorporating the excluded volume of macroion hard cores. The partial structure factors \( S_{\mu\nu}(k) \) are related in turn to the Fourier transforms of the pair correlation functions \( h_{\mu\nu}(r) \):

\[ S_{\mu\nu}(k) = x_{\mu} \left[ \delta_{\mu\nu} + n_{\nu} h_{\mu\nu}(k) \right], \]

(29)

where \( x_{\mu} \) is the concentration of microion species \( \mu \). In Fourier space, \( h_{\mu\nu}(k) \) is related to the direct correlation function \( \hat{c}_{\mu\nu}(k) \) via the Ornstein-Zernike integral equation

\[ \hat{h}_{\mu\nu}(k) = \hat{c}_{\mu\nu}(k) + \sum_{\lambda} n_{\lambda} \hat{c}_{\mu\lambda}(k) \hat{h}_{\lambda\nu}(k). \]

(30)

For a weakly coupled plasma, whose average Coulomb energy is much lower than the average thermal energy, we can approximate the direct correlation functions by their asymptotic limits \( \hat{c}_{\mu\nu}(k) \approx -\beta\hat{\rho}_{\mu\nu}(k) = z_{\mu} z_{\nu} \hat{c}(k) \), where \( \hat{c}(k) = -4\pi \lambda_B / k^2 \) and \( \lambda_B = e^2/\epsilon k_B T \) is the Bjerrum length, defined as the separation between two elementary charges \( e \) at which the electrostatic potential energy equals the typical thermal energy \( k_B T \). Further assuming \( \hat{h}_{\mu\nu}(k) = z_{\mu} z_{\nu} \hat{h}(k) \), it follows that

\[ \hat{h}_{\mu\nu}(k) = \frac{z_{\mu} z_{\nu} \hat{c}(k)}{1 - n_0 \hat{c}(k)}, \]

(31)

with \( n_0 \equiv \sum_{\mu} z_{\mu}^2 n_{\mu} \). Combining Eqs. (28)-(31), we obtain the linear response functions

\[ \chi_{\mu}(k) = -\frac{\beta z_{\mu} n_{\mu}}{1 + \kappa^2/k^2}, \]

(32)

where the inverse Debye screening length is defined as \( \kappa \equiv \sqrt{4\pi \lambda_B n_0} \). We emphasize that \( \kappa \) here incorporates the macroion excluded volume, since \( n_0 \) involves the microion densities \( n_{\mu} \) in the free volume, i.e., the volume not excluded by the macroion hard cores. Thus, our definition of \( \kappa \) is larger than the conventional definition by a factor of \( 1/\sqrt{T - \eta} \). With Eq. (32), the effective electrostatic interactions now can be explicitly calculated.

B. Effective pair potentials and volume energy

The general expressions derived for the effective pair potentials and volume energy apply to any type of spherical macroion, provided only that the macroion-microion interaction can be factorized as \( v_{\mu\nu}(r) = Z_m z_{\mu} v_m(r) \). For separations exceeding the macroion radius (assuming point microions), \( v_{\mu\nu}(r) \) is of Coulomb form. For colloidal macroions with an impenetrable core, the potential inside the core may be chosen [32, 54] to ensure exclusion of microions from the core:

\[ \beta v_m(r) = \lambda_B \left\{ \begin{array}{ll} \frac{1}{r}, & r > a_m \\ \frac{\alpha_m}{a_m} - \frac{1}{r}, & r < a_m \end{array} \right. \]

(33)

where the constant \( \alpha_m \) can be fixed to impose the condition \( \rho_m(r) = 0 \) for \( r < a_m \). With the appropriate choice of \( \alpha_m = \kappa a_m/(1 + \kappa a_m) \), Eq. (33) has the Fourier transform

\[ \beta \hat{v}_m(k) = \frac{4\pi \lambda_B}{k^2} \frac{1}{1 + \kappa a_m} \left[ \cos(\kappa a_m) + \frac{\sin(\kappa a_m)}{\kappa} \right]. \]

(34)

Next, substitution of Eqs. (32) and (34) into Eq. (21) yields the Fourier transform of the microion-induced pair potential

\[ \beta \hat{v}_{mn,\text{ind}}(k) = -Z_m Z_n \frac{\beta^2 \kappa^2}{4\pi \lambda_B} \frac{k^2}{k^2 + \kappa^2} \hat{v}_m(k) \hat{v}_n(k), \]

(35)

with an inverse transform

\[ \beta v_{mn,\text{ind}}(r) = \begin{cases} B_{mn} \exp\left[-\frac{\kappa}{\kappa r}(r - a_m - a_n)\right] - \beta v_{mn}(r), & r \geq a_m + a_n \\ B_{mn} \left\{ \begin{array}{l} \frac{-\kappa}{2} (a_m + a_n - |a_m - a_n|) - 1, \quad r \leq |a_m - a_n| \\ \frac{-\kappa}{4} \left[ r + \frac{(a_m - a_n)^2}{r} \right] - 2(a_m + a_n) \right\} - 1, \quad |a_m - a_n| < r < a_m + a_n \end{array} \right. \]

(36)

with

\[ B_{mn} \equiv Z_m Z_n \kappa \lambda_B / [(1 + \kappa a_m)(1 + \kappa a_n)]. \]

Substituting this result for the induced pair potentials into Eq. (27), we finally obtain effective macroion-macroion
pair potentials (for $r \geq a_m + a_n$)

$$\beta v_{mn,\text{eff}}(r) = Z_m Z_n \lambda_B \frac{\exp[\kappa(a_m + a_n)]}{(1 + \kappa a_m)(1 + \kappa a_n)} \frac{\exp(-\kappa r)}{r}.$$  

(37)

Thus, we recover the Yukawa pair potential of Eq. [5], with the prefactor determined to be

$$A_{mn} = Z_m Z_n \frac{\epsilon^2}{\kappa} \frac{\exp[\kappa(a_m + a_n)]}{(1 + \kappa a_m)(1 + \kappa a_n)}.$$  

(38)

The effective pair potentials of Eq. (37) are the same as those predicted by the DLVO theory extended to mixtures in the dilute limit, i.e., by solving the linearized Poisson-Boltzmann equation with free boundary conditions. Our result applies also, however, at nonzero macroion concentrations — as long as the linear response approximation remains valid — in which case the screening constant depends on both salt and macroion densities and incorporates the macroion excluded volume.

Similar results for effective pair potentials in colloidal mixtures have been derived by Ruiz-Estrada et al. [16] using integral-equation theory. Starting from the primitive model, and contracting the Ornstein-Zernike equation (relating pair and direct correlation functions) to eliminate explicit reference to the direct correlation functions between microions, these authors obtain a formal expression for effective direct correlation functions between macroions. Making a mean spherical approximation (MSA) for all correlation functions, they obtain an analytical expression of the same general Yukawa form as Eq. (5). The effective pair potentials derived from the MSA [Eqs. (2.15) and (2.16) in Ref. [16]] differ, however, from ours [Eq. (37)] in two respects. First, the prefactors are different, the MSA result reducing to our $A_{mn}$ only in the dilute limit. Second, the MSA expression for the screening constant [Eq. (2.7) in Ref. [16]], like that in the DLVO theory, does not incorporate the macroion excluded volume.

Beyond effective pair potentials, the linear response approach also consistently yields a one-body volume energy. By substituting Eqs. (37)-(39) into Eq. (25), we arrive at an explicit result for the volume energy of a colloidal mixture:

$$\beta E_0 = \beta F_p - \frac{\lambda_B}{2} \sum_{m} \frac{N_m Z_m^2}{a_m + \kappa} - \frac{1}{2} \left( \sum_{m} \frac{Z_m N_m}{\kappa} \right)^2.$$  

(39)

Assuming a weakly coupled microion plasma, the first term on the right-hand side can be approximated as the free energy of an ideal gas of microions:

$$\beta F_p \simeq \sum_{\mu} N_{\mu} \left[ \ln(n_{\mu} \Lambda_{\mu}^3) - 1 \right],$$  

(40)

$\Lambda_{\mu}$ being the thermal wavelength of microion species $\mu$. The second term on the right-hand side of Eq. (39) represents the self energy of the macroions embedded in the microion plasma. A similar expression for the volume energy of colloidal mixtures can be derived from the DFT approach to effective interactions [30]. Our result for $E_0$ differs, however, in the manner in which macroion excluded volume is incorporated via the screening constant.

V. STRUCTURE AND THERMODYNAMICS

A. Pair structure of binary mixtures

To validate the linear response theory and assess the accuracy of the predicted effective pair potentials, we performed molecular dynamics (MD) simulations of the coarse-grained model (with implicit microions). Using the LAMMPS package [82], we computed macroion-macroion radial distribution functions (RDFs) $g_{ij}(r)$ and compared with available results from Monte Carlo (MC) simulations [28] of a binary mixture of oppositely charged ($Z_+ = -Z_- = 5$), equally sized ($\sigma_+ = \sigma_- = 3$ nm) colloids at equal volume fractions ($\eta_+ = \eta_- = 0.005319$).

For convenience, in our MD simulations, we replaced the hard-sphere interactions between macroions with the repulsive part of the Lennard-Jones pair potential, $v_{LJ}(r) = 4\epsilon_{LJ} \left[ (\sigma_{LJ}/r)^{12} - (\sigma_{LJ}/r)^6 \right]$, and cut and shifted to zero at its minimum, which we matched to the diameter of the colloids: $\sigma_c = 2^{1/6} \sigma_{LJ}$. We set $\epsilon_{LJ} = 5000$ kcal/mol, checking that higher values did not significantly affect the RDFs, and cut and shifted to zero the effective pair potentials [Eq. (37)] at $r_{\text{cut}} = 20/\kappa$, beyond...
which range the interactions are negligible.

Starting from initial configurations of 4000 particles on a face-centered cubic lattice, with appropriate concentrations of each species, we performed simulations in the canonical ensemble at fixed temperature \( T = 298 \, \text{K} \) with periodic boundary conditions in a cubic simulation box of side length \( L \) chosen to ensure that \( L/2 > r_{\text{cut}} \). Following an initial equilibration phase, we sampled configurations and collected statistics at regular intervals over \( 10^6 \) time steps.

As seen in Fig. 2, the macroion-macroion RDFs calculated for this system from our simulations of the coarse-grained model are in excellent agreement with those obtained from MC simulations of the primitive model. We caution, however, that the electrostatic coupling in this system, characterized by \( Z\lambda_B/\sigma = 1.2 \), is relatively weak. Preliminary comparisons indicate that more strongly coupled systems \( (Z\lambda_B/\sigma > 3) \) must be modeled using effective macroion charges consistently derived from charge renormalization theory \cite{83}.

To demonstrate an application to a mixture that is bidisperse in both size and charge, and to explore the influence of nanoparticles on the structure of colloids, we performed an MD simulation of a mixture with relatively large size and charge asymmetries. Specifically, we simulated the coarse-grained model of a salt-free aqueous suspension of \( N_1 = 500 \) colloids, of radius \( a_1 = 50 \, \text{nm} \) and valence \( Z_1 = 100 \), and \( N_2 = 1500 \) nanoparticles, of radius \( a_2 = 5 \, \text{nm} \) and valence \( Z_2 = 10 \), at volume fractions \( \eta_1 = 0.2 \) and \( \eta_2 = 0.0006 \) [from Eqs. (37) and (38)]. Curves represent (left to right) \( \beta v_{12,\text{eff}}(r) \) (dotted-dashed) \( \beta v_{11,\text{eff}}(r) \) (dashed), and \( \beta v_{11,\text{eff}}(r) \) (solid). The dotted curve is the effective pair potential of the one-component model (OCM) of the same suspension in the absence of the smaller macroions (species 2).

**B. Pressure and equation of state**

The pressure of a colloidal mixture can be computed from the Helmholtz free energy \( F \) via \( p = -\langle \partial F/\partial V \rangle_{N,m,N_s} \), where the subscripts denote fixing of all macroion and salt ion numbers (fixed \( T \) is implied). Equivalently, \( p = n^2 \langle \partial F/N/\partial n \rangle_{x_m,x_s} \), where \( N \) and \( n = N/V \) are the total macroion number and number density, \( x_m = N_m/N \) is the concentration of macroion species \( m \), and \( x_s = N_s/N \) is the salt concentration.

The Helmholtz free energy of the system naturally divides into two parts, \( F = E_0 + F_m \), where \( E_0 \) is the volume energy arising from tracing out the microion degrees of freedom and \( F_m \) is the free energy associated with effective interactions between macroions. Correspondingly, the pressure can be separated as \( p = p_0 + p_m \), where the volume energy contribution \cite{39} is given by

\[
\beta p_0 = n^2 \beta \left( \frac{\partial (E_0/N)}{\partial n} \right)_{x_m,x_s}
\]

\[
= \sum_m n_m \beta \frac{\kappa\lambda_B}{4(1-\eta)} \frac{m_m Z^2}{(m + \kappa a_m)^2} \tag{41}
\]

and the macroion contribution is given by

\[
\beta p_m = \sum_m n_m - \beta \left( \frac{\partial U}{\partial V} \right)_{x_m,x_s} \tag{42}
\]

Here \( n_m = N_m/V \) denotes the number density of...
macroion species \( m \) and

\[
U = \sum_{m} \sum_{i<j}^{N_m} v_{mm,\text{eff}}(r_{ij}) + \sum_{m<n}^{N_m} \sum_{i=1}^{N_n} v_{mn,\text{eff}}(r_{ij}) \tag{43}
\]

is the potential energy associated with macroion pair interactions. The ensemble average of \( \partial U/\partial V \) can be approximated by either a perturbation theory or molecular simulations, taking into account the dependence of the effective pair potentials on the macroion and salt densities \( \xi_{11}^0 \). As shown in the Appendix, this density dependence results in extra terms in addition to the usual virial term. Taken together, Eqs. (11) and (22) can be used to calculate the pressure of a polydisperse colloidal suspension or polyelectrolyte solution.

Finally, to illustrate the significance for thermodynamic properties of the excluded-volume correction to the effective interactions, we examine the volume energy contribution \( p_0 \) [Eq. (11)] to the total osmotic pressure of the colloidal-nanoparticle mixture described in Sec. V A (see caption to Fig. 4). Figure 5 shows the concentration dependence of \( p_0 \), both with and without excluded volume taken into account. Evidently, with increasing macroion concentration, the excluded-volume correction increasingly affects the osmotic pressure, which in turn can influence thermodynamic phase behavior.

VI. CONCLUSIONS

In summary, we have presented a theory of effective electrostatic interactions for polydisperse suspensions of charged macroions, thus generalizing to mixtures a theory previously developed for monodisperse suspensions. Within a coarse-graining framework that integrates out macroion degrees of freedom, we derived general expressions for effective macroion-macroion pair potentials and a one-body volume energy. The theory is based on a linear response approximation for the macroion densities and a mean-field random phase approximation for macroion structure that neglects all but long-range macroion correlations. For model mixtures of charged hard-sphere colloids, we have presented explicit analytical expressions for the effective interactions. These expressions should be accurate for suspensions of weakly correlated (monovalent) microions and macroions whose charges are sufficiently low that electrostatic coupling strengths are below the threshold for charge renormalization.

The resulting effective pair potentials have the same Yukawa form as predicted by linearized Poisson-Boltzmann theory and integral-equation theories. Our expressions are somewhat more general, however, by incorporating macroion density and excluded volume via the Debye screening constant. As a quantitative test of accuracy, we have calculated structural properties from molecular dynamics simulations of the coarse-grained model, taking the effective pair potentials as input. Radial distribution functions of binary mixtures of oppositely charged colloidal macroions are found to agree closely with corresponding results from Monte Carlo simulations of the primitive model. For a highly asymmetric (colloid-nanoparticle) mixture, our results demonstrate that nanoparticles can enhance electrostatic screening, thus weakening pair correlations, in suspensions of charged colloids. Assessing the range of validity of the theory will require further comparisons with primitive model simulations and experiments.
The one-body volume energy, which depends on the average density of the macroions, can influence the phase behavior and other thermodynamic properties, especially in deionized suspensions. For binary colloidal mixtures, our analytical expression for the volume energy is similar to that derived from density-functional theory [30], but incorporates macroion excluded volume in a different manner. The volume energy also is an essential element required to extend to mixtures the charge renormalization theory previously developed for monodisperse colloidal suspensions [73, 74].

A subject for future work is the application of the effective interaction theory developed here to explore the structure and thermodynamic phase behavior of macroion mixtures, including colloid-nanoparticle mixtures, distinguished by extreme size and charge asymmetries [83]. Particularly interesting would be an investigation of the possibility of electrostatically driven bulk phase separation in deionized suspensions and a generalization to mixtures of a previously proposed charge renormalization theory [73, 74], which can significantly extend the range of validity of coarse-grained models to mixtures of highly charged macroions.

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Appendix A: Pressure calculation

For our coarse-grained model of colloidal mixtures, the virial theorem for the pressure must be generalized to account for the density-dependence of the effective pair potentials [74]. To this end, the ensemble average in Eq. (12) can be written more explicitly as

$$\left\langle \frac{\partial U}{\partial V} \right\rangle_{x_n x_s, \{r\}} = - \left\langle \frac{\partial \mathcal{V}_{int}}{3 V} \right\rangle_{x_n x_s, \{r\}} + \left\langle \frac{\partial U}{\partial V} \right\rangle_{x_n x_s, \{r\}} ,$$

where the first term on the right-hand side involves the usual internal virial $\mathcal{V}_{int}$, and the partial derivative in the last term is taken for a fixed configuration of macroions $\{r\}$. For a mixture, the internal virial is

$$\mathcal{V}_{int} = \sum_{m} \sum_{i<j} \sum_{j} (1 + \kappa r_{ij}) \nu_{mm,eff}(r_{ij})$$

$$+ \sum_{m<n} \sum_{i=1}^{N_m} \sum_{j=1}^{N_n} (1 + \kappa r_{ij}) \nu_{mn,eff}(r_{ij}) .$$

Noting that $U$ depends implicitly on the volume through $\kappa$, we can write

$$\left\langle \frac{\partial U}{\partial V} \right\rangle_{x_n x_s, \{r\}} = \left\langle \frac{\partial U}{\partial \kappa} \right\rangle_{\{r\}} \left\langle \frac{\partial \kappa}{\partial V} \right\rangle_{N_m, N_s} ,$$

where

$$\left\langle \frac{\partial \kappa}{\partial V} \right\rangle_{N_m, N_s} = - \frac{\kappa}{2V(1-\eta)}$$

and

$$\left\langle \frac{\partial U}{\partial \kappa} \right\rangle_{\{r\}} = \sum_{m} \sum_{i<j} f_m(r_{ij}) \nu_{mm,eff}(r_{ij})$$

$$+ \sum_{m<n} \sum_{i=1}^{N_m} \sum_{j=1}^{N_n} f_{mn}(r_{ij}) \nu_{mn,eff}(r_{ij})$$

with

$$f_m(r_{ij}) = \frac{2\kappa a_m^2}{1 + \kappa a_m} - r_{ij}$$

and

$$f_{mn}(r_{ij}) = \frac{\kappa[a_m^2 + a_n^2 + \kappa(a_m + a_n)a_m a_n]}{(1 + \kappa a_m)(1 + \kappa a_n)} - r_{ij} .$$

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