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Effective forces between macroions in highly charged colloidal suspensions

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It is shown based on the systematic theory recently developed for charge-stabilized colloidal suspensions of interacting Brownian particles with Coulomb interactions that the effective force between highly charged colloidal macroions can be written as

$$\mathbf{F}^{\mathrm{eff}}(r)=k_BTZ^2l_B^2\{Z^2\exp[-(Z/q)^{1/2}r/\lambda_D]-q^2\exp(-r/\lambda_D)\}(\mathbf{r}/r^4),$$

where $\lambda_D=(4\pi n_c q^2 l_B)^{-1/2}$ is the Debye screening length, Ze the charge of macroions, $-qe$ the charge of counterions, l_B the Bjerrum length, and n_c the number density of counterions. This force consists of two parts. The first part results from the long-range, Coulomb interactions between macroions and is repulsive over a short range of distances between macroions. The second part results from the pair correlations due to the long-range, Coulomb interactions between macroions and counterions and is attractive over a broad range of distances between macroions. This force is expected to describe the ordering phenomena in highly charged colloidal suspensions. [S1063-651X(99)50903-3]

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In recent years, there has been considerable experimental and theoretical interest in an understanding of the mechanism for ordering in charged colloids [1]. Charge-stabilized colloidal suspensions have been found experimentally to exhibit a rich variety of crystalline, liquidlike, and amorphous phases [2,3]. Many theoretical investigations to understand these phase behavior have been done by using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [4]. For the last decade, however, there has been growing evidence for the existence of a long-range, attractive interaction between macroions [2,5], which cannot be explained by the DLVO theory. There are several proposals for an explanation of that attractive interaction (see, for example, [6]). In this paper, we propose an effective potential that has an attractive minimum at long interparticle distances, based on the systematic theory recently developed for highly charged colloidal suspensions [7]. Thus, we show that the pair correlation due to many-body, long-range Coulomb interactions between macroions and counterions leads to an effective, long-range attractive force, while the pair correlation due to many-body, long-range Coulomb interactions between macroions leads to an effective, short-range repulsive force.

We consider a three-dimensional charged colloidal particles suspended in a polar solvent. In the following, we restrict ourselves to the simple case in which the concentration of added salt is ignored. Thus, the system consists of two ionized spherical particles in an incompressible fluid with viscosity η and the static dielectric constant ε: the macroions of radius a, mass m, charge Ze, and position vector $\mathbf{X}_i(t)$ $(i=1,2,\ldots,N_m)$ with the number density $n_m=N_m/V$, and the counterions of radius a_c, mass m_c, and charge $-qe$ with the number density $n_c=N_c/V$, where V is the total volume of the system. Here the global charge neutrality requires that $Zn_m=qn_c$. In the absence of added salt, one can assume the following pair interaction potentials $V_{mm}(r)$, $V_{mc}(r)$, $V_{cc}(r)$ between macroions and counterions [8]: $\beta V_{mm}(r)=Z^2l_B/r$ for $r>2a$ and ∞ for $r\leqslant 2a$, $\beta V_{mc}(r)=-Zql_B/r$ for $r>a+a_c$ and ∞ for $r\leqslant a+a_c$, and $\beta V_{cc}(r)=q^2l_B/r$, for $r>2a_c$ and ∞ for $r\leqslant 2a_c$, where r is the interparticle distance, $l_B=e^2/\varepsilon k_BT$ the Bjerrum length, and $\beta=1/k_BT$. In the following, we also restrict ourselves to the special case where $a/a_c\gg 1$, $m/m_c\gg 1$, and $Z/q\gg 1$. Hence, it is a reasonable approximation to neglect the size of counterions as compared to that of macroions, i.e., to treat the counterions as pointlike particles with $a_c=0$. The fluctuating velocity field of the fluid is assumed to be described by the fluctuating, linear Navier-Stokes equation, supplemented by stick boundary conditions at the surfaces of the spheres.

For simplicity, in the following we neglect the hydrodynamic interactions between macroions since their effects are small for large Z [7]. Then, the system has two macroscopic characteristic lengths: a and $\lambda_D=(4\pi n_c q^2 l_B)^{-1/2}=a/(3\phi\Gamma)^{1/2}$, where $\phi=4\pi a^3 n_m/3$ is the volume fraction of macroions, and $\Gamma=Zql_B/a$ the dimensionless coupling parameter between macroions and counterions. For highly charged suspensions, therefore, we have three characteristic times: the relaxation time of the momentum contained in the fluid volume of size a, $\tau_f\sim\rho a^2/\eta$; the Brownian relaxation time of macroions, $\tau_B\sim m/(6\pi\eta a)$; the structural relaxation time, $\tau_s\sim a^2/D_0$, which is a time required for a macroion to diffuse over a distance a, where ρ is the fluid mass density, and D_0 the single-macroion diffusion coefficient. For large Z, we have $\lambda_D\gg a$, and $\tau_s\gg\tau_B\gg\tau_f$. Depending on the space-time scales, therefore, there are two characteristic stages: a kinetic stage (K) where the space-time cutoff $(x_{\mathrm{cutoff}},t_{\mathrm{cutoff}})$ is set as $\lambda_D\gg x_{\mathrm{cutoff}}\gg a$ and $\tau_B\gg t_{\mathrm{cutoff}}\gg\tau_f$, and a suspension-hydrodynamic stage (SH), where $x_{\mathrm{cutoff}}\gg\lambda_D$ and $\tau_s\geqslant t_{\mathrm{cutoff}}\gg\tau_B$. In the following, we only discuss the SH stage.

Let us define the single-macroion number density by

$$N(\mathbf{r},t)=\sum_{i=1}^{N_m}\delta(\mathbf{r}-\mathbf{X}_i(t)). \tag{1}$$

Then, the number density $N(\mathbf{r},t)$ can be split up into the average number density $n(\mathbf{r},t)=\overline{N(\mathbf{r},t)}$ and a fluctuating

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part $\delta N(\mathbf{r},t)$ as $N(\mathbf{r},t)=n(\mathbf{r},t)+\delta N(\mathbf{r},t)$, where the bar denotes an average over a suitable initial ensemble. As was shown in Ref. [7], in the SH stage on the time scale of order τ_S, the diffusion equation for $n(\mathbf{r},t)$ can be written, up to lowest order in ∇ and ϕ, as

$$\frac{\partial}{\partial t}n(\mathbf{r},t)=D_0\nabla^2 n(\mathbf{r},t)-D_0\boldsymbol{\nabla}\cdot\mathbf{C}(\mathbf{r},t) \tag{2}$$

with the correlation term of order $\phi^{1/2}$,

$$\begin{aligned}\mathbf{C}(\mathbf{r}_1,t)=\beta\biggl\{\int d\mathbf{r}_2\,\theta(|\mathbf{r}_{12}|-2a)\mathbf{F}_{12}^{mm}H^{mm}(\mathbf{r}_1,\mathbf{r}_2,t)\\ +\int d\mathbf{r}_2^c\,\theta(|\mathbf{r}_1-\mathbf{r}_2^c|-a)F_{12}^{mc}H^{mc}(\mathbf{r}_1,\mathbf{r}_2^c,t)\biggr\},\end{aligned} \tag{3}$$

where $\mathbf{r}_i^c$ denotes the position of counterion i, $\mathbf{F}_{ij}^{mm}$ and $\mathbf{F}_{ij}^{mc}$ the Coulomb forces between macroions and counterions, and $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$. Here the step function $\theta(r)$ arises from the fact that the particles are supposed to be nonoverlapping; $\theta(r)=1$ for $r\geqslant 0$ and $\theta(r)=0$ for $r<0$. The term $H^{mm}(\mathbf{r}_1,\mathbf{r}_2,t)$ represents the pair correlation function between macroions separated by a distance of order λ_D, while the term $H^{mc}(\mathbf{r}_1,\mathbf{r}_2^c,t)$ represents the pair correlation function between macroions and counterions separated by a distance of order λ_D. The functions $H^{mm}(\mathbf{r}_1,\mathbf{r}_2,t)$ and $H^{mc}(\mathbf{r}_1,\mathbf{r}_2^c,t)$ obey, to lowest order in $\boldsymbol{\nabla}_2$, $\boldsymbol{\nabla}_2^c$, and ϕ,

$$\begin{aligned}\frac{\partial}{\partial t}H^{mm}(\mathbf{r}_1,\mathbf{r}_2)=D_0(1+e_{12})\biggl\{&\boldsymbol{\nabla}_2^2H^{mm}(\mathbf{r}_1,\mathbf{r}_2)\\ &-\beta\boldsymbol{\nabla}_2\biggl[\mathbf{F}_{21}^{mm}n(r_2)n(\mathbf{r}_1)\\ &+\int d\mathbf{r}_3^c\mathbf{F}_{23}^{mc}n^c(\mathbf{r}_2^c)H^{mc}(\mathbf{r}_1,\mathbf{r}_3^c)\\ &+\int d\mathbf{r}_3\mathbf{F}_{23}^{mm}n(\mathbf{r}_2)H^{mm}(\mathbf{r}_1,\mathbf{r}_3)\biggr]\biggr\},\end{aligned} \tag{4}$$

$$\begin{aligned}\frac{\partial}{\partial t}H^{mc}(\mathbf{r}_1,\mathbf{r}_2^c)=D_0^c(1+e_{12})\biggl\{&\boldsymbol{\nabla}_2^{c2}H^{mc}(\mathbf{r}_1,\mathbf{r}_2^c)\\ &-\beta\boldsymbol{\nabla}_2^c\biggl[\mathbf{F}_{21}^{cm}n^c(\mathbf{r}_2^c)n(\mathbf{r}_1)\\ &+\int d\mathbf{r}_3\mathbf{F}_{23}^{cm}n^c(\mathbf{r}_2^c)H^{mm}(\mathbf{r}_1,\mathbf{r}_3)\\ &+\int d\mathbf{r}_3^c\mathbf{F}_{23}^{cc}n^c(\mathbf{r}_2^c)H^{mc}(\mathbf{r}_1,\mathbf{r}_3^c)\biggr]\biggr\}\\ &+O(D_0/D_0^c),\end{aligned} \tag{5}$$

where D_0^c is the single-counterion diffusion coefficient with $D_0^c=(a/a_c)D_0(\geqslant D_0)$, $n^c(\mathbf{r}_2^c,t)$ the average number density of the counterions, e_{ij} the exchange operator between i and j, and $\boldsymbol{\nabla}_2^c=\partial/\partial\mathbf{r}_2^c$. Here we should note that the last term of Eq. (4) screens the long-range interactions between macroions with the length of order $(q/Z)^{1/2}\lambda_D$, while the last term of Eq. (5) screens the long-range interactions between a macroion and a counterion with the length of order λ_D. Here we should note that in order to derive Eq. (3), we have neglected the terms due to the short-range interactions between macroions since they lead only to corrections at small volume fractions.

We next discuss the asymptotic solutions of Eqs. (4) and (5) in the SH stage, where the length scale $|\mathbf{r}_1|$ of interest is longer than λ_D, and the time scale is of order τ_S, while the interparticle distances, $|\mathbf{r}_1-\mathbf{r}_2|$ and $|\mathbf{r}_1-\mathbf{r}_2^c|$, are of order λ_D. On the length scale longer than λ_D, one can further expand $n(\mathbf{r}_2,t)$ and $n^c(\mathbf{r}_2^c,t)$ about $\mathbf{r}_1$. Since $D_0/D_0^c=a_0/a\ll 1$, the dynamics of the counterions surrounding the macroions follows the motion of the macroions in this stage. Hence, one can also assume that $n^c(\mathbf{r},t)\simeq(Z/q)n(\mathbf{r},t)$. Since we can put $\partial H^{mm}/\partial t=\partial H^{mc}/\partial t\simeq 0$ on the time scale of order τ_S, from Eqs. (4) and (5), we thus find, to lowest order in $\boldsymbol{\nabla}$ and q/Z,

$$\begin{aligned}H^{mm}(\mathbf{r}_1,\mathbf{r}_2,t)=-\frac{Zql_B}{r_{12}}\left(\frac{Z}{q}\right)^2\exp[-r_{12}/\lambda_m(r_1,t)]n(\mathbf{r}_1,t)\\ \times(1+\mathbf{r}_{21}\cdot\boldsymbol{\nabla}_1)n(\mathbf{r}_1,t),\end{aligned} \tag{6}$$

$$\begin{aligned}H^{mc}(\mathbf{r}_1,\mathbf{r}_2^c,t)=\frac{Zql_B}{|\mathbf{r}_1-\mathbf{r}_2^c|}\exp[-|\mathbf{r}_1-\mathbf{r}_2^c|/\lambda(r_1,t)]n(\mathbf{r}_1,t)\\ \times\{1+(\mathbf{r}_2^c-\mathbf{r}_1)\cdot\boldsymbol{\nabla}_1\}n(\mathbf{r}_1,t),\end{aligned} \tag{7}$$

with the screening length

$$\lambda(\mathbf{r},t)=[4\pi n(\mathbf{r},t)Zql_B]^{-1/2}=a/[3\Phi(\mathbf{r},t)\Gamma]^{1/2}, \tag{8}$$

where $\Phi(\mathbf{r},t)=(4\pi/3)a^3n(\mathbf{r},t)$ denotes the local volume fraction of macroions, and $\lambda_m(r,t)=(q/Z)^{1/2}\lambda(r,t)$. Use of Eqs. (3), (6), and (7) then leads to

$$\begin{aligned}\mathbf{C}(\mathbf{r}_1,t)=(Zl_B)^2\int d\mathbf{r}_2\,\theta(r_{12}-2a)\frac{\mathbf{r}_{12}}{r_{12}^4}\\ \times[Z^2\exp\{-r_{12}/\lambda_m(r_1,t)\}\\ -q^2\exp\{-r_{12}/\lambda(r_1,t)\}]\\ \times n(\mathbf{r}_1,t)\mathbf{r}_{21}\cdot\boldsymbol{\nabla}_1n(\mathbf{r}_1,t).\end{aligned} \tag{9}$$

Although the contribution from the term H^{mm} can be negligible for large Z, we have retained it in Eq. (9) to find a reasonable force which should be valid not only for the long distance but also for the short distance. For large Z, one can obtain $\mathbf{C}(\mathbf{r},t)\simeq\Gamma^{3/2}\sqrt{3\Phi(\mathbf{r},t)}\boldsymbol{\nabla}n(\mathbf{r},t)$. Use of Eq. (2) then leads to the nonlinear deterministic diffusion equation for $n(\mathbf{r},t)$ in the absence of the hydrodynamic interactions between macroions

$$(\partial/\partial t)n(\mathbf{r},t)=\nabla\cdot[D_S(\Phi(\mathbf{r},t))\boldsymbol{\nabla}n(\mathbf{r},t)] \tag{10}$$

with the self-diffusion coefficient $D_S(\Phi)=D_0[1-\Gamma^{3/2}\sqrt{3\Phi}]$, which leads to the glass transition volume fraction $\phi_g=(1/3)\Gamma^{-3}$. Here we note that as was shown in Ref. [7], ϕ_g is slightly modified by the hydrodynamic interactions.

We now discuss the effective forces. Let $\mathbf{F}^{\rm eff}(r_{ij},t)$ denote the effective force between macroions i and j at time t. In the absence of hydrodynamic interactions, one can then write the Langevin equations for the position of macroion i, on the timescale of order τ_S, as

$$\frac{d}{dt}\mathbf{X}_i(t)=D_0\sum_{j(\neq i)}^{N_m}\beta\mathbf{F}^{\rm eff}(|\mathbf{X}_{ij}(t)|,t)+\mathbf{R}_i(t), \tag{11}$$

where $\mathbf{X}_{ij}(t)=\mathbf{X}_i(t)-\mathbf{X}_j(t)$, and $\mathbf{R}_i(t)$ represents the Gaussian, Markov random force and satisfies

$$\begin{gathered}\langle\mathbf{R}_i(t)\rangle=0,\\ \langle\mathbf{R}_i(t)\mathbf{R}_j(t')\rangle=2D_0\delta(t-t')\,\delta_{i,j}\mathbf{1}.\end{gathered} \tag{12}$$

By taking the time derivative of Eq. (1) and then using Eq. (11), we obtain

$$\begin{aligned}\frac{\partial}{\partial t}n(\mathbf{r}_1,t)=&D_0\nabla_1^2 n(\mathbf{r}_1,t)-D_0\nabla_1\cdot\int d\mathbf{r}_2\,\theta(r_{12}\\&-2a)\mathbf{F}^{\rm eff}(r_{12},t)[n(\mathbf{r}_1,t)n(\mathbf{r}_2,t)\\&+G_2(\mathbf{r}_1,\mathbf{r}_2,t)],\end{aligned} \tag{13}$$

where the pair correlation function between macroions, G_2, is given by

$$G_2(\mathbf{r}_1,\mathbf{r}_2,t)=\overline{\delta N(\mathbf{r}_1,t)\,\delta N(\mathbf{r}_2,t)}-\delta(\mathbf{r}_1-\mathbf{r}_2)n(\mathbf{r}_1,t). \tag{14}$$

Here we should note that in order to derive the first term of Eq. (13), we have averaged out the terms including the random force by employing the formulation introduced by the present author [9] and retained the terms up to order ∇^2.

The pair correlation function G_2 obeys the same equation as Eq. (4) without the term related to the counterions, except that H^{mm} and $\mathbf{F}_{12}$ are now replaced by G_2 and $\mathbf{F}^{\rm eff}$, respectively. On the length scale longer than λ_D, therefore, G_2 can be safely negligible compared to the leading term $n(\mathbf{r}_1,t)n(\mathbf{r}_2,t)$ in Eq. (13) for large Z since it is screened by the length of order λ_m ($\ll\lambda_D$), similar to Eq. (6). By comparing Eq. (2) with Eq. (9) to Eq. (13), we thus find

$$\begin{aligned}\mathbf{F}^{\rm eff}(r_{12},t)=&k_BTZ^2l_B^2[Z^2\exp\{-r_{12}/\lambda_m(r_1,t)\}\\&-q^2\exp\{-r_{12}/\lambda(r_1,t)\}](\mathbf{r}_{12}/r_{12}^4).\end{aligned} \tag{15}$$

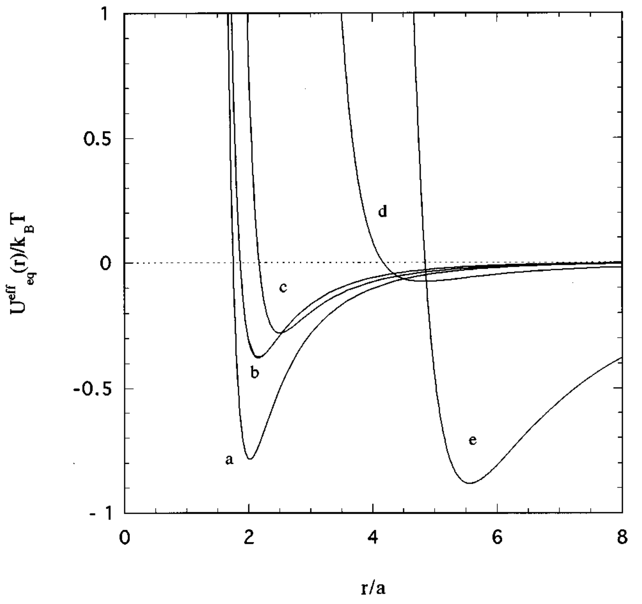

FIG. 1. Effective potential $U^{\rm eff}_{\rm eq}(r)$ in units of k_BT vs r in units of a for different suspension parameters (Z,ϕ); (a) (360, 0.0074), (b) (280,0.01), (c) (280,0.0074), (d) (280,0.002), and (e) (900,0.0002), where the other parameters are chosen as $q=1$, $a=55.4$ nm, and $l_B=7.29$ Å at $T=293$ K.

The first term of Eq. (15) is repulsive over a short range of order λ_m, while the second term is attractive over a broad range of order λ. Since $\mathbf{F}^{\rm eff}(r_{12},t)$ is the conservative force, one can also find the potential energy $U(r_{12},t)$ through the relation $\mathbf{F}^{\rm eff}(r_{12},t)=-\nabla_{12}U^{\rm eff}(r_{12},t)$ as

$$\begin{aligned}U^{\rm eff}(r_{12},t)=&\frac{1}{2}k_BTZ^2l_B^2\\&\times\Bigg[Z^2\Bigg\{\left(\frac{1}{r_{12}}-\frac{1}{\lambda_m(r_1,t)}\right)\frac{\exp[-r_{12}/\lambda_m(r_1,t)]}{r_{12}}\\&-\frac{1}{\lambda_m(r_1,t)^2}E_i[-r_{12}/\lambda_m(r_1,t)]\Bigg\}\\&-q^2\Bigg\{\left(\frac{1}{r_{12}}-\frac{1}{\lambda(r_1,t)}\right)\frac{\exp[-r_{12}/\lambda(r_1,t)]}{r_{12}}\\&-\frac{1}{\lambda(r_1,t)^2}E_i[-r_{12}/\lambda(r_1,t)]\Bigg\}\Bigg],\end{aligned} \tag{16}$$

where $E_i(-x)=-\int_x^\infty e^{-s}/s\,ds$. Because of the long-range attractive term in addition to the repulsive term, the effective potential can have an attractive minimum at long interparticle distances, depending on the values of Z and ϕ. Here we note that if the system is initially out of equilibrium, both effective force and potential depend on space and time through $\Phi(\mathbf{r},t)$, whose time evolution is described by Eq. (10).

For long times, the system reaches the equilibrium state where $\Phi(\mathbf{r},\infty)=\phi$. Hence, we have $\lambda(\mathbf{r},\infty)=\lambda_D$ and $\lambda_m(\mathbf{r},\infty)=(q/Z)^{1/2}\lambda_D$. In Fig. 1 we show the equilibrium potential energy $U^{\rm eff}_{\rm eq}(r)$, where the parameters are chosen as $q=1$, $a=55.4$ nm and $l_B=7.29$ Å at $T=293$ K [10]. The depth of the potential well becomes large and the minimum position of the potential decreases either as Z increases with fixed ϕ (see curves a and c) or as ϕ increase with fixed Z (see curves b, c, and d). Even for sufficiently dilute suspensions, the depth can be finite if Z is large enough (see curve e). Hence, several phase behavior would be expected to exist since the macroions can get trapped in the potential well, depending the values of Z and ϕ.

In conclusion, we have found the effective force given by Eq. (15) and also the effective potential given by Eq. (16) for highly charged colloidal suspensions. The correlations among macroions and counterions separated by a distance of order λ_D have been shown to be an origin of the long-range, attractive interactions between macroions. This effective potential is thus expected to explain the experimental observations which suggest a long-range attractive interaction. The Brownian dynamics simulation of Eq. (11) is now in progress. The ordering phenomena in charged colloidal suspensions with the effective force $\mathbf{F}^{\text{eff}}(r,t)$ will be discussed elsewhere.

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