

Fluctuations and ordering in macroion suspensions

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We calculate the static properties of macroion density fluctuations in both bulk and in confined, strongly interacting, macroion suspensions (macroions interact via the Derjaguin-Landau-Verwey-Overbeek potential) in terms of a simple density-functional *ansatz*. We show how to map a strongly interacting suspension to a weakly interacting one and obtain the renormalized charge, diameter and scattering structure factors analytically. The model is extrapolated to predict crystalline order in terms of a Hansen-Verlet-type of criterion as well as an effective hard-sphere crystallization condition, and good agreement with simulations is found. The increase in correlations observed in recent experiments in two, confined layers is demonstrated.

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Recent measurements of the interaction potential U between an isolated, highly charged macroion pair *in the bulk* [1,2] unambiguously demonstrate the validity of the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential even in the range where $U \gg k_B T$, provided that an effective charge [3] Z is properly chosen. Under certain circumstances near a charged wall, the long-range part of the potential was shown to be attractive and to deviate from the DLVO form [2,4,5]; however, its shorter-range repulsive part may still be well described by the DLVO potential. A related set of recent measurements deals with the crystallization of colloidal suspensions in the bulk [1,6] and under confinement [7–9]. An important feature of these experiments is the ability to measure the structural properties of the suspension at the level of a single macroion. These observations provide the data necessary for testing theories of the macroion interactions under three limiting conditions: (i) ultra low packing fractions of macroions $10^{-2} \sim 10^{-5}$; (ii) highly deionized environment $\sim 10^{-6}$ M of salt; (iii) high charge Z of the macroions $10^3 \sim 10^4$. In this paper, we provide analytical results to characterize the density correlations of 3D and confined suspensions under these conditions. The model is extrapolated to predict the ordering instability and the liquid-solid coexistence line in the framework of the Hansen-Verlet (HV) [10] and an effective hard-sphere [11] crystallization criterion, and good agreement with the experimental observations [6,9] is found. The increase in correlations observed in recent experiments in two, confined layers [9] is demonstrated.

We begin by proposing a procedure for mapping a strongly interacting system of colloidal particles to a weakly interacting one. The idea of renormalizing the interaction potential by rescaling the macroion diameter was explored in the past by Hansen and Hayter [12] using the mean-spherical approximation (MSA) [13]. In our approach, we renormalize both the diameter d and the charge Z [14] of the macroions using a physical criterion that is different from that of Ref. [12] (see below). This allows us to obtain a simple analytical expression for the structure factor of strongly interacting colloidal suspensions in both 3D and quasi-2D, as well as for the renormalized parameters d^* and Z^* . These analytical results (in particular, the quasi-2D system, which is not tractable within the MSA approach [12]) may be used for the

predictions of the macroion interactions in complex geometries such as confined macroion suspensions.

We first focus on the structural properties of 3D suspension and then discuss confined suspensions, i.e., quasi-2D layers of mobile, negatively charged macroions. The system is characterized by an average number density n_m (number of macroions per unit volume of 3D suspension) and σ (per unit area of quasi-2D layer), respectively, a particle diameter d and a charge number Z [14]. The macroions are embedded in a solvent with a uniform dielectric constant ϵ and screened by three-dimensional, mobile positive counterions and binary salt ions with average volume number densities n_c and n_s , respectively; for simplicity, both the counterions and the salt ions are assumed to be monovalent and pointlike, since their size is negligible compared to the macroion radius. Later on, we consider the case of two interacting macroion layers. In what follows, we treat suspensions in both 3D and quasi-2D, as effectively one-component systems consisting of macroions interacting via a screened Coulomb potential [15].

The free energy of a dilute system may be represented as a sum of the entropy and the interaction free energy of species [13,16]:

$$F = \int \sigma(r) [\ln(\sigma(r)v_0) - 1] d\vec{r} + \frac{1}{2} \int \sigma(r)\sigma(r') [1 - e^{-V(|\vec{r}-\vec{r}'|)}] d\vec{r} d\vec{r}', \quad (1)$$

where $V(r) = U(r)$, if $r > d$ and $V(r) = \infty$, if $r \leq d$; here $U(r)$ is the soft part of the pair interaction potential. All energies are given in the units of $k_B T$, and $\sigma(r) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i)$ is the number density of species; N and d are the total number and the diameter of the particles, respectively; \vec{r} is a D -dimensional vector; $\delta(\vec{r})$ stands for the D -dimensional Dirac delta function; and v_0 is a constant with the dimensions of a volume. The Gaussian fluctuation contribution ΔF to the free energy F may be obtained in terms of the Fourier transform of the fluctuations of the densities [17]: $\delta\sigma(\rho) = \sigma(\rho) - \sigma$, where σ is the average number density of the species:

$$\Delta F = \frac{1}{2} \sum_k \delta\sigma(\vec{k}) \delta\sigma(-\vec{k}) \left[\frac{1}{\sigma} + B(k) \right], \quad (2)$$

here $B(k) = \int e^{i\vec{k}\vec{r}} (1 - e^{-V(r)}) d\vec{r}$. Our main objective is to predict the structure factors, $S(\vec{k}) = \langle \delta\sigma(\vec{k}) \delta\sigma(-\vec{k}) \rangle / \sigma$ (the averaging is performed with the distribution function $\sim e^{-\Delta F/k_B T}$). The amplitude and the position k^* of the peak of the structure factor allow one to estimate the strength and the characteristic length-scale of the density fluctuations in the liquid state. In general, even within the density functional (DF) *ansatz*, the structure factor must be calculated numerically.

We now show that one can renormalize the diameters of the species d and the amplitudes of the interaction potentials U in order to *effectively reduce* the interaction energy per particle in such a way that the free energy, Eq. (1), may be represented in the simple linearized form:

$$F^* = \int \sigma(r) [\ln(\sigma(r)v_0) - 1] d\vec{r} + \frac{1}{2} \int_{|\vec{r}-\vec{r}'| \leq d^*} \sigma(r)\sigma(r') d\vec{r} d\vec{r}' + \frac{1}{2} \int_{|\vec{r}-\vec{r}'| > d^*} \sigma(r)\sigma(r') U^*(|\vec{r}-\vec{r}'|) d\vec{r} d\vec{r}', \quad (3)$$

where the non-local second term represents the hard-core interactions [18]; here d^* is the renormalized diameter and U^* is the potential U in which the charge Z and the diameter d are renormalized. This linearization allows the structure factor to be calculated analytically; it is very useful when colloids in complex geometries are considered.

The macroion-macroion interaction potential $U(r)$ is approximated by the DLVO potential [15] that effectively accounts for the screening of the macroions by the salt and counterions:

$$U(r) = \frac{Z^2 \ell_B}{(1 + \kappa d/2)^2} \frac{e^{-\kappa(r-d)}}{r}, \quad (4)$$

where $\ell_B = e^2/(ek_B T) \approx 7 \text{ \AA}$ is the Bjerrum length in water, and κ is the inverse Debye screening radius of the *microions* (the salt ions plus counterions) [19]: $\kappa^2 = 4\pi\ell_B(2n_s + n_c) = 8\pi\ell_B n$; below we refer to $n = (n_s + n_c/2)$, as the salt concentration; and d is the diameter of the macroion. We note that since the DLVO potential is derived as a solution of the linearized Poisson-Boltzmann (PB) equation within the linear superposition approximation, the renormalization procedure, besides enabling to obtain analytical results for the structure factors (see below), assures the validity of the DLVO potential itself [3].

In order to map a *strongly interacting* solution of macroions of size d and charge Z to a *weakly interacting* one with renormalized size d^* and charge Z^* , we impose two physical conditions to find d^* and Z^* : (i) the requirement that at the distance of closest approach the spheres with renormalized charge and size interact with an energy $k_B T$; (ii) the requirement that the electrostatic potential around an isolated macroion in the renormalized suspension should be unchanged for $r > d^*$:

$$U^*(Z^*, d^*, r = d^*) = 1, \quad (5)$$

$$\Psi(Z, d, r) = \Psi^*(Z^*, d^*, r), \quad r \geq d^*, \quad (6)$$

where $\Psi(Z, d, r) = Z e e^{-\kappa(r-d/2)} / [\epsilon r (1 + \kappa d/2)]$ is the DLVO electrostatic potential around an isolated macroion. The condition, Eq. (5), can be derived variationally as follows: It is easy to see that the second virial coefficient of the reference suspension, $B = \int_{r \leq d} d\vec{r} + \int_{r > d} (1 - e^{-U(r)}) d\vec{r}$ is *always* smaller than B^* of the renormalized system: $B^* = \int_{r \leq d^*} d\vec{r} + \int_{r > d^*} U^*(r) d\vec{r}$. The opposite is true for the corresponding compressibilities: $S(0) > S^*(0)$. The condition, Eq. (5), is obtained minimizing the thermodynamic fluctuation free energy $\mathcal{G}^* = \int D \delta\sigma e^{-\Delta F^*}$ with respect to d^* , where ΔF^* is derived analogously to Eq. (2); this is also equivalent to the minimizing the difference between the corresponding compressibilities, $\min |S(0) - S^*(0)|$.

As a result, we find d^* as a solution of the following algebraic equation, identical for both 3D suspensions and quasi-2D layers:

$$d^* = d + \frac{1}{\kappa} \ln \left[\frac{Z^2 \ell_B}{d^* (1 + \kappa d/2)^2} \right], \quad (7)$$

and Z^* is obtained from Eq. (6). This allows us to obtain analytical expressions for the structure factor in the quasi-2D case (see below), which is impossible within the MSA framework [12]. The criteria we use, Eqs. (5) and (6), are different from the criterion used by Hansen and Hayter [12], $g(d^*) = 1$, where $g(r)$ is the radial distribution function. We emphasize, that our approach [i.e., both the DF *ansatz*, Eq. (1), and the results of the renormalization procedure for d^* and Z^*] is valid when the effective packing fraction of the suspension ($\phi^* = n_m \pi d^{*3}/6$, in 3D, where n_m is the volume density of macroions; and $\phi^* = \sigma \pi d^{*2}/4$, in 2D, where σ is the surface density of macroions) is small: $\phi^*, \varphi^* \ll 1$. The last criterion ensures that the macroion suspension is dilute enough to be dominated by the two-body interactions; in practice, one can use a somewhat weaker criterion of validity: $\phi^* \leq 0.5$ and $\varphi^* \leq 0.8$, where the numbers 0.5 and 0.8 correspond to the critical packing fractions of the liquid-solid transition in a hard-sphere and a hard-disk system, respectively [11].

We emphasize again that the renormalized charge Z^* and diameter d^* are obtained from the DLVO potential in which the charge Z has a meaning of an effective charge [3]. In Ref. [3] Alexander and co-workers solved numerically the nonlinear PB equation for the spherically symmetric counterion distribution around the macroion. They demonstrated that the Debye-Huckel solution of the linearized PB equation provides an excellent approximation for the exact solution, provided the charge on the colloidal particle is replaced by the *effective charge* which is always less than the actual (titratable) charge on the macroion. This effective charge Z takes into account nonlinear screening effects in the vicinity of the macroion surface omitted in the linearized PB equation from which the DLVO potential is derived. As the direct measurements show [1,2], the DLVO potential with the effective charge Z can be used to fit the experiments at such interparticle separations r where the energy $U(r)$ is as large as

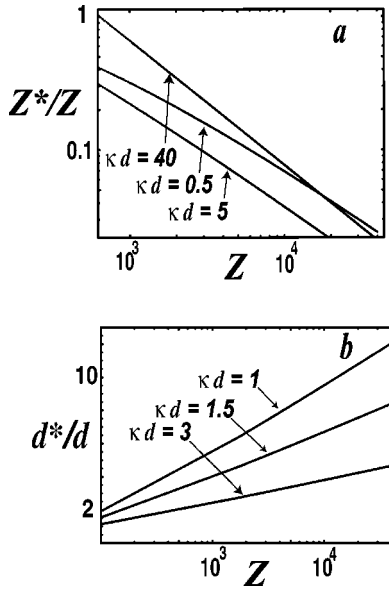


FIG. 1. Dependence of the renormalized macroion charge Z^* (a), and diameter d^* (b), as a function of Z for different salt concentration regimes, $d=650$ nm.

$U \sim 10 k_B T$. At smaller separations, the DLVO potential is not valid (since the linear superposition approximation within which it is obtained breaks down), however, this does not influence our DF ansatz, since large repulsive interactions, e.g., $U \sim 10 k_B T$ and $U \sim 100 k_B T$ have the same effect on the free energy, since in both cases in Eq. (1), $(1 - e^{-U/k_B T}) \approx 1$, i.e., the interaction acts as an effective hard-core potential. This is exactly what our rescaling procedure does: it transforms all the interactions, where $U > k_B T$ to the hard-core interactions. This procedure makes the DLVO potential accurate for the renormalized macroion suspension at all inter-particle separations; most importantly, it allows us to treat the soft part of the renormalized potential $U^*(r)$ at $r \geq d^*$ perturbatively.

One can identify four asymptotic regimes for d^* and Z^* with respect to the amount of the added salt κd : (i) zero salt regime, $\kappa d \ll 1$: $d^* \approx Z^2/\ell_B$, $Z^* \approx Z$; (ii) ultra-low salt regime, $\kappa d < 1$: $\kappa d^* \approx \ln Z^2 - \ln(d^*/\ell_B)$, $Z^* \approx (d^*/\ell_B)^{1/2}(1 + \kappa d^*/2)$; (iii) low salt regime, $\kappa d > 1$: $\kappa d^* \approx \kappa d + \ln Z^2 - \ln(d^*/\ell_B) - \ln(\kappa d/2)^2$, $Z^* \approx (d^*/\ell_B)^{1/2} \kappa d^*/2$; (iiii) high salt regime, $\kappa d \gg 1$: $d^* \approx d$, $Z^* \approx Z$. We note that the experimental parameters used in the recent measurements of macroion interactions [2,9] correspond to our regime (iii). The dependence of the renormalized d^* and Z^* as a function of Z for different salt regimes is represented in Fig. 1. Z^* gets significantly renormalized compared to Z , while d^* is equal to just a few times d for a wide range of experimental parameters [2,9], e.g., if $d=650$ nm, $Z=7300$, $\kappa^{-1}=275$ nm, then $d^* \approx 4.36d$ and $Z^* \approx 391$. This is easily understood from the analytical expression for d^* , where the deviations from d are only logarithmic. With increasing salt concentration d^* always decreases for fixed d and Z , while $Z^* \approx Z$ for extremely low (zero) $\kappa d \ll 1$, and for very high, $\kappa d \gg 1$, salt concentrations; Z^* is most significantly renormalized when $\kappa d \sim 1$, i.e., within the range of salt concen-

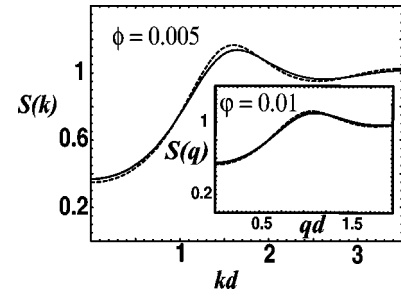


FIG. 2. Structure factor $S(k)$ of 3D suspension (solid line) from the DF ansatz compared with $S^*(k)$ obtained using the renormalization procedure (dashed line), where $d=650$ nm, $Z=6000$, $\kappa^{-1}=200$ nm, $\phi=0.005$. Inset: Structure factor of the quasi-2D macroion layer $S(q)$ from the DF ansatz compared with $S^*(q)$ obtained using the renormalization procedure (dashed line), where $d=650$ nm, $Z=7300$, $\kappa^{-1}=270$ nm, $\phi=0.01$.

trations $\sim 10^{-6}$ M relevant to the experiments [1,2,9].

We now predict the behavior of the macroion-macroion structure factors, $S(k)$ and $S^*(k)$, in the suspension and analyze how they evolve with the volume fraction of the suspension, $\phi = n_m \pi d^3/6$, and with the amount of the added salt characterized by κ . In our model $S^*(k)$ acquires an especially simple form:

$$S^*(k) = \left[1 + 24\phi \left(\mathcal{W}(k) + \frac{\kappa d^* \cos \kappa d^* + \kappa d^* \sin \kappa d^*}{k d^{*3} (k^2 + \kappa^2)} \right) \right]^{-1}, \quad (8)$$

where $\mathcal{W}(k) = [\sin \kappa d^* - \kappa d^* \cos \kappa d^*]/(\kappa d^*)^3$ is the form-factor of the effective hard sphere system of diameter d^* . Note, that the charge Z enters $S^*(k)$ only through the renormalized diameter d^* . The adopted renormalization of d^* and Z^* predicts a structure factor $S^*(k)$ in good agreement with $S(k)$ defined by Eq. (2). This is shown in Fig. 2; as one decreases ϕ to values, ≤ 0.01 , one obtains excellent agreement between $S(k)$ and $S^*(k)$; i.e., the renormalized system, described by d^* and Z^* has macroion density correlations that are very similar to those in the reference system, including the height of the peak of $S(k)$, and the characteristic length-scale, characterized by the position of the peak k^* .

We now show that the two-body DF fluctuation ansatz we adopt allows one to predict the liquid-solid coexistence line in the colloidal suspension based on the HV crystallization criterion. In the fluid phase, the structure factor shows oscillations as a function of the wave-vector; when ϕ approaches a critical value ϕ_c , the principal peak of $S(k)$ grows and reaches its maximum $S_{\max}(k_c)$ at a particular value of the wave-vector k_c [20]. In order to test the ability to predict the liquid-solid coexistence in terms of $S_{\max}(k_c)$ using the HV criterion, we compare the liquid-solid coexistence line obtained by the computer simulation study of the hard-core Yukawa model of Ref. [21] for $\kappa d=5$, with the coexistence line obtained with the HV criterion, $S_{\max}(k_c) \approx 1.9$ in Fig. 3. One observes good coincidence between the curves. We note

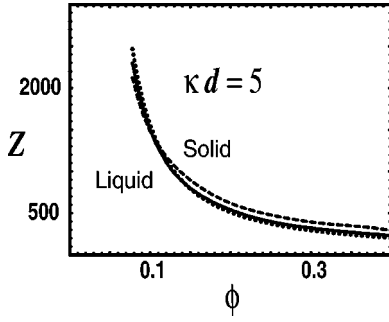


FIG. 3. Liquid-solid coexistence line obtained using the HV crystallization criterion, with $S_{\max} \approx 1.9$ (solid line) compared with the coexistence line obtained from computer simulations of the hard-core Yukawa model [21] (dashed line). The coexistence line obtained with the effective hard-sphere crystallization criterion (see the text) for $\phi_c^* \approx 0.73$ (dotted line) coincides almost perfectly with the line obtained using the HV criterion.

that the HV criterion for the Lennard-Jones system predicts the crystallization transition at $S_{\max} \approx 2.85$ [10]; for the Yukawa system it is $S_{\max} \approx 3.2$ [22]. It is interesting to note, that if one considers the macroions as the hard spheres with the diameter d^* , which exhibit the hard-sphere liquid-solid transition [11] at the certain value of critical packing fraction ϕ_c^* , one observes very good agreement with the coexistence curve obtained using the HV criterion, if one takes $\phi_c^* \approx 0.73$, see Fig. 3. Assuming that the ordered phase is similar in its structure to the properties of the liquid phase at the instability, we can extrapolate from the ordering fluctuations an estimate of the lattice constant of the emerging crystal state by associating the lattice constant with the wave-length of the first oscillation mode $2\pi/k_c$. Taking reasonable parameters [1,6], e.g., $d = 650$ nm, $Z = 6000$, $\kappa^{-1} = 200$ nm, we find that $S(k)$ reaches its threshold value, $S_{\max}(k_c) \approx 1.9$, at $\phi_c \approx 0.02$, and $\lambda_c = 2\pi/k_c \approx 3.8d$, both of the numbers are in a very good agreement with the experimental ones [1,6]. Our model estimates unambiguously reproduce one of the principal features of the observed crystals—extremely low packing densities.

In what follows we concentrate on the problem of the macroion fluctuations within a quasi-2D layer and on the interaction of two such fluctuating macroion layers; this is relevant to recent experiments [9] on the formation of the metastable macroion crystallites in the bulk and near the surface. We show that the inter-layer interactions lead to enhanced macroion ordering fluctuations and may promote a crystallization transition within a layer. In the liquid state, far away from the ordering transition, we obtain simple expressions for the structure factors for a few, experimentally accessible limits. The fluctuations within an isolated macroion layer $D=2$ are described analogously to the 3D colloidal suspension outlined above, the renormalization of d^* and Z^* holds true in this case, as well. The comparison of the DF two-body structure factor $S(q)$ versus the renormalized, approximate $S^*(q)$ is represented in the inset of Fig. 2, where $\vec{q} = (k_x, k_y, 0)$ two-dimensional wave-vector. One again observes good agreement which becomes better upon further dilution of the system (reducing the surface density of mac-

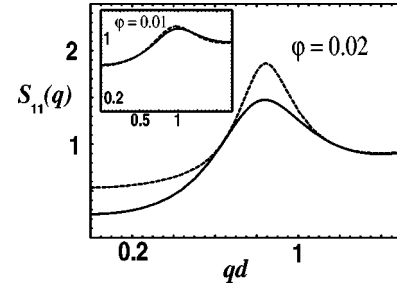


FIG. 4. $S_{11}(q)$ in the case of one quasi-2D macroion layer in the vicinity of another layer $h \approx d$ (dashed line) compared with $S_{11}(q)$ (solid line) for an isolated layer, $h \gg d$, where $d = 650$ nm, $Z = 6000$, $\kappa^{-1} = 400$ nm, $\varphi = 0.02$; the enhancement of the intra-layer correlations induced by the interaction with another layer is observed. Inset (same axes): Intra-layer structure factor, $S_{11}(q)$ of the double-layer system (solid line) from the DF *ansatz* compared with $S^*(q)$ obtained using the renormalization procedure (dashed line), where $d = 650$ nm, $Z = 6000$, $\kappa^{-1} = 325$ nm, $\varphi = 0.01$, and $h = d$.

roions, $\varphi = \sigma\pi d^2/4$). In the limit of very low salt $\kappa d \ll 1$, one can obtain an analytical expression for $S^*(q)$ using our procedure:

$$S^*(q) = \left[1 + 8\varphi^* \frac{J_1(qd^*)}{qd^*} + \frac{\omega(qd^*)}{q\lambda_D} \right]^{-1}, \quad (9)$$

where $\omega(x) = 1 - xJ_0(x) + (\pi/2)x[J_0(x)\mathbf{H}_1(x) - J_1(x)\mathbf{H}_0(x)]$, here J_0 , J_1 and \mathbf{H}_0 , \mathbf{H}_1 are the Bessel and Struve functions, respectively; $\varphi^* = \sigma\pi d^{*2}/4$, and $\lambda_D^{-1} = 2\pi/\ell_B Z^2 \sigma$ is a 2D analog of the Debye screening length; $S^*(q \rightarrow 0) = [1 + 4\varphi^* + 1/(q\lambda_D)]^{-1}$. We note, that the very low salt regime, $\kappa d \ll 1$, where Eq. (9) is valid, is experimentally accessible for the nanometer-scale size colloidal particles or charged micelles under ultra-low salt concentrations, $10^{-6} - 10^{-7}$ M; we also note that the concentration of the particles should be so low, as to satisfy the practical criterion of applicability of the model, $\varphi^* < 1$. In the case of finite κd , the compressibility, $S^*(0)$ has a simple form:

$$S^*(0) = \left[1 + 4\varphi^* \left(1 + \frac{1}{\kappa d^*/2} \right) \right]^{-1}. \quad (10)$$

From Eq. (10) one can extract d^* ; this expression can be tested by measurements of the scattering in the long-wavelength limit (see e.g., Ref. [1,6]).

In the case of two interacting, symmetric layers of macroions separated by a distance h , we can reformulate Eqs. (1)–(3) to include *two interacting components* that are the macroions on each layer interacting via the DLVO potential; here we outline the renormalization procedure for the double-layer system. The interaction free energy F_{12}^* of the renormalized double-layer system is

$$\begin{aligned}
F_{12}^* &= F_1^* + F_2^* + \int_{|\vec{\rho}-\vec{\rho}'| \leq \sqrt{d^{*2}-h^2}} \sigma_1(\rho) \sigma_2(\rho') d^2 \rho d^2 \rho' \\
&+ \int_{|\vec{\rho}-\vec{\rho}'| > \sqrt{d^{*2}-h^2}} \sigma_1(\rho) \sigma_2(\rho') \\
&\times U_{12}^*(|\vec{\rho}-\vec{\rho}'|) d^2 \rho d^2 \rho', \quad (11)
\end{aligned}$$

if $h \leq d^*$. If $h > d^*$, the third term in Eq. (11) is absent and in the fourth term, the integration is performed over the whole space. F_1^* and F_2^* are given by Eq. (3), with the substitution $\sigma \rightarrow \sigma_1$ and $\sigma \rightarrow \sigma_2$, respectively; the third and the fourth terms in Eq. (11) correspond to the *renormalized* hard-core and the *renormalized* soft part of the inter-layer interaction, respectively. The inter-layer potential U_{12} is given by Eq. (4), provided that one substitutes $e^{-\kappa\rho/\rho} \rightarrow e^{-\kappa\sqrt{\rho^2+h^2}/\sqrt{\rho^2+h^2}}$. In the limit $h \gg d$, the double-layer system reduces to the case of 2 independent layers. The renormalization procedure analogous to Eqs. (5) and (6) leads again to d^* , given by Eq. (7); the main observation here is that d^* is independent of the inter-layer spacing h ; the plot of $S_{11}(q)$ vs. $S_{11}^*(q)$ is shown in the inset of Fig. 4. In the very low salt concentration limit, $\kappa d \ll 1$, for large inter-layer distance h , one finds:

$$S_{11}^*(q) = \frac{S^*(q)}{1 - [S^*(q)e^{-qh/(q\lambda_D)}]^2}, \quad \kappa d \ll 1, h \gg d^*, \quad (12)$$

where $S^*(q)$ is given by Eq. (9). We note again, that the renormalization procedure we adopt is applicable for the double-layer macroion system within the regime $\varphi^* < 1$, where the magnitude of the ordering fluctuations is below the crystallization threshold; however, we may extrapolate the DF *ansatz*, to predict the ordering transition in the double-layer system as we did for 3D. In Fig. 4 we show the intra-layer structure factor $S_{11}(q)$ for two interacting layers vs. $S_{11}^*(q)$ for an isolated layer $h \gg d$. The principal observation is that upon reducing the inter-layer distance h , the intra-layer structure factor $S_{11}(q)$ grows and may reach its crystallization threshold even if φ within an isolated layer is lower than the critical value of the surface fraction φ_c . Taking the reasonable parameters [9]: $Z = 6000$, $d = 650$ nm, $\kappa^{-1} = 400$ nm, and using the Hansen-Verlet criterion with $S_{11}^{\max}(q_c) \sim 2$, we obtain that the double-layer system crystallizes at $\varphi_c \approx 0.02$, while an isolated layer, $h \gg d$, crystallizes only at a higher packing fraction of $\varphi_c \approx 0.03$. We note that in the recent experiments of Grier and Larsen [9] a similar mechanism was suggested to be responsible for the stabilization of the crystal state of the macroion layers distant from the walls of the confining glass cell. In that case, however, the effective interaction between the colloidal particles was shown to deviate from the DLVO form close to the walls.

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