ELSEVIER

Physica B 228 (1996) 78–82

PHYSICA B

Interparticle interactions and crystallization transition in charged colloidal suspensions

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Abstract

The interaction between charged colloidal particles is known to be dominated by Coulomb interactions which are screened by the microscopic counterions. For highly diluted systems linear screening theory leads to the familiar DLVO (Derjaguin–Landau–Verwey–Overbeek) pair potential between spherical suspensions. For concentrated suspensions, however, nonlinear screening effects resulting in effective counterion-induced many-body forces between the macroparticles become important. An "ab initio" theory is discussed which fully describes these nonlinear effects. Furthermore, some results for freezing of charged colloidal suspensions are presented both in three and two spatial dimensions.

Keywords: Interparticle interactions; Crystallization transition; Colloidal suspension

1. Introduction

Monodisperse suspensions of spherical macroparticles in a microscopic solvent represent excellent representations of simple one-component liquids on a mesoscopic length scale [1]. In particular, a concentrated suspension exhibits similar structural correlations than that of convenient classical liquids. For high density (resp. low temperature), a fluid suspension freezes into a regular crystal of macroparticles. Once the effective interparticle forces between the colloidal macroparticles are known, one can proceed along the same way as known for classical fluids in order to predict the phase diagram, etc., using classical statistical mechanics. These interparticle forces include a term stemming from the van-der-Waals attraction as well as a repulsive force needed to stabilize the colloidal suspension against irreversible coagulation. For sterically stabilized suspensions, the repulsive forces are conveniently written in terms of a simple excluded volume term. For charged suspensions, the Coulomb interaction is responsible for the repulsive forces. These Coulombic forces, however, are screened by the microscopic counterions and by added salt ions. In general, the counterion screening is a highly nonlinear effect leading to effective counterion-induced many-body forces between the charged colloidal particles (macroions) but in many cases a Yukawa form for the interaction pair potential is sufficient to describe the interaction. The aim of this paper is to review some important recent developments in the theoretical description of the effective interactions between the charged macro-particles as well as to summarize some aspects of the crystallization transition in colloidal suspensions. As far as details are concerned, the reader is referred to the original papers.

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PII S0921-4526(96)00343-2

2. Effective interactions of charged colloidal suspensions

2.1. The "primitive" model

Most of the theoretical work starts from the so-called "primitive model". In this model, the solvent merely enters into the theory as a continuum screening the electric interaction by its dielectric constant ε, i.e. the discrete nature of the solvent particles is neglected. The microscopic counterions carrying charge $-qe$, on the other hand, are fully taken into account. Furthermore, the macroions are characterized by a core-radius R and a total charge Ze. The "primitive model" is a combination of excluded volume and Coulomb forces. Its pair potentials read:

$$v_{\mathrm{mm}}(r) = \begin{cases} \infty & \text{for } r \leqslant 2R, \\ \frac{Z^2e^2}{\varepsilon r} & \text{for } r > 2R, \end{cases} \tag{1}$$

$$v_{\mathrm{mc}}(r) = \begin{cases} \infty & \text{for } r \leqslant R, \\ -\frac{Zqe^2}{\varepsilon r} & \text{for } r > R, \end{cases} \tag{2}$$

$$v_{\mathrm{cc}} = \frac{q^2e^2}{\varepsilon r}, \tag{3}$$

where the indices m and c are for macroions and counterions, respectively. If n_{m} and n_{c} are the numbers of macroions and counterions per unit volume, global charge neutrality requires that

$$Zn_{\mathrm{m}} = qn_{\mathrm{c}}. \tag{4}$$

For given values of Z, q, R and ε, the equilibrium properties of the suspension depend on the temperature T and the number density n_{m}, n_{c} being determined by the constraint (4).

Due to the strong charge asymmetry $Z \gg q$ in the primitive model, it is very difficult to access the static correlations of the macroions by theory or by direct computer simulation. It has been proved useful to integrate out the counterionic degrees of freedom [2]. They one arrives at an effective Hamiltonian for the macroions defined by

$$\begin{aligned} H_{\mathrm{eff}} &= -k_{\mathrm{B}}T \ln(\langle \exp(-H/k_{\mathrm{B}})T\rangle_{\mathrm{c}}) \\ &= K_{\mathrm{m}} + V_{\mathrm{mm}} + \mathscr{F}([\rho_{\mathrm{c}}(\boldsymbol{r})]; \{\,'\,\}). \end{aligned} \tag{5}$$

Here k_{B} is Boltzmann's constant, H is the total Hamiltonian of the primitive model and $\langle\cdots\rangle_{\mathrm{c}}$ denotes a canonical average with respect to the counterions. Furthermore, K_{m} is the kinetic energy of the macroions and

$$V_{\mathrm{mm}} = \sum_{i<j} v_{\mathrm{mm}}(|\boldsymbol{R}_i - \boldsymbol{R}_j|) \tag{6}$$

is the potential energy due to the direct macroion–macroion interaction $\{\boldsymbol{R}_i\}$ denoting the macroion positions. Finally, $\mathscr{F}$ is the canonical free energy of the counterions in the external field $V_{\mathrm{ext}}(\boldsymbol{r}, \{\boldsymbol{R}_j\})$ made up by the macroions. It is known [1] that $\mathscr{F}$ can be represented as a *functional* of the local counterion density field $\rho_{\mathrm{c}}(\boldsymbol{r})$ depending additionally parametrically on the macroion positions $\{\boldsymbol{R}_i\}$. Conveniently, $\mathscr{F}$ can be split into a sum of four terms as follows:

$$\mathscr{F} = \mathscr{F}_{\mathrm{id}} + \mathscr{F}_{\mathrm{ext}} + \mathscr{F}_{\mathrm{cc}} + \mathscr{F}_{\mathrm{corr}}, \tag{7}$$

where

$$\mathscr{F}_{\mathrm{id}} = k_{\mathrm{B}}T \int \mathrm{d}\boldsymbol{r}\, \rho_{\mathrm{c}}(\boldsymbol{r})[\ln(\Lambda_{\mathrm{c}}^3\rho_{\mathrm{c}}(\boldsymbol{r})) - 1], \tag{8}$$

$$\begin{aligned} \mathscr{F}_{\mathrm{ext}} &= \int \mathrm{d}\boldsymbol{r}\, \rho_{\mathrm{c}}(\boldsymbol{r}) V_{\mathrm{ext}}(\boldsymbol{r}, \{\boldsymbol{R}_j\}) \\ &= \sum_j \int \mathrm{d}\boldsymbol{r}\, \rho_{\mathrm{c}}(\boldsymbol{r}) v_{\mathrm{mc}}(|\boldsymbol{r} - \boldsymbol{R}_j|), \end{aligned} \tag{9}$$

$$\mathscr{F}_{\mathrm{cc}} = \frac{q^2e^2}{2\varepsilon} \iint \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \frac{\rho_{\mathrm{c}}(\boldsymbol{r})\rho_{\mathrm{c}}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{10}$$

In the "ideal" part (8), Λ_{c} is the de Broglie thermal wavelength of the counterions; $\mathscr{F}_{\mathrm{ext}}$ describes the coupling of the latter to the macroions, while $\mathscr{F}_{\mathrm{cc}}$ is a mean-field contribution stemming from the Coulomb repulsion between counterions.

What one sees directly is that $\mathscr{F}$ depends *nonlinearly* on $\{\boldsymbol{R}_i\}$ since the equilibrium density $\rho_{\mathrm{c}}^{(0)}(\boldsymbol{r})$ obtained by minimizing $\mathscr{F}$ with respect to $\rho_{\mathrm{c}}(\boldsymbol{r})$

$$\left.\frac{\delta\mathscr{F}}{\delta\rho_{\mathrm{c}}}\right|_{\rho_{\mathrm{c}}=\rho_{\mathrm{c}}^{(0)}(\boldsymbol{r})} = 0 \tag{11}$$

depends implicitly on $\{\boldsymbol{R}_i\}$. In particular, this dependence will be nonquadratic. This immediately implies that there effective *many-body forces* between the macroions induced by nonlinear counterion screening.

Up to now, the expression for H_{eff} is exact. If one would know an explicit expression for $\mathscr{F}_{\mathrm{corr}}$, one could use this effective Hamiltonian to calculate

static macroion–correlations exactly. Unfortunately, however, one does not know the explicit form of the correlation functional $\mathscr{F}_{\text{corr}}$ and one has to rely on approximations which are discussed now further.

2.2. Linear screening: the DLVO-potential

The simplest approximation is to neglect $\mathscr{F}_{\text{corr}}$ completely and to perform a quadratic expansion in the density around the mean density n_c which is a valid procedure for weak inhomogeneities (e.g. for highly diluted macroions):

$$\mathscr{F}_{\text{id}} \cong F_0 + \int d\boldsymbol{r}\{k_B T\{\ln(\Lambda^3 n_c)[\rho_c(\boldsymbol{r}) - n_c] + \frac{k_B T}{2n_c}[\rho_c(\boldsymbol{r}) - n_c]^2\}. \quad (12)$$

For pointlike macroions the minimizing equilibrium counterion density can be found analytically [2] being a linear superposition of screened Coulomb (or Yukawa) orbitals:

$$\rho_c^{(0)}(\boldsymbol{r}, \{\boldsymbol{R}_i\}) = \sum_i \frac{Z}{q}\frac{\kappa^2}{4\pi}\frac{\exp(-\kappa|\boldsymbol{r} - \boldsymbol{R}_i|)}{|\boldsymbol{r} - \boldsymbol{R}_i|}, \quad (13)$$

where

$$\kappa^2 = \frac{4\pi q^2 e^2 n_c}{\varepsilon k_B T} \quad (14)$$

is the Debye–Hückel screening constant. In this case the effective interaction between the macroions is pairwise with the effective pair potential [2]

$$v_{\text{mm}}^{\text{eff}}(r) = \frac{Z^2 e^2}{\varepsilon r}\exp(-\kappa r). \quad (15)$$

If the macroions have a finite core additional of radius R additional approximations again lead to an effective Yukawa pair potential where Z has to be replaced by

$$Z_{\text{eff}} = \frac{Z\exp(\kappa R)}{1 + \kappa R} \quad (16)$$

resulting in the famous DLVO-expression for the electrostatic part of the interaction between the macroions. Consequently, the quadratic expansion is equivalent to linear screening in the spirit of Debye–Hückel theory. However, for moderate macroion concentrations, the Debye–Hückel theory breaks down.

2.3. Nonlinear screening: Many-body forces

If one treats $\mathscr{F}_{\text{id}}$ exactly avoiding the quadratic expansion but again neglects $\mathscr{F}_{\text{corr}}$ completely then one gets the familiar Poisson–Boltzmann theory. It can easily be shown that the resulting equations for the minimizing density and the effective macroionic forces are equivalent to Poisson's equation in electrostatics and Boltzmann's equations in thermodynamics. On this level, counterion-induced many-body forces between the macroions are present. A computer simulation based on Poisson–Boltzmann theory was recently performed by Fushiki [3] to obtain the macroion pair correlations.

A better approximation is to adopt the local density approximation for $\mathscr{F}_{\text{corr}}$:

$$\mathscr{F}_{\text{corr}} = k_B T \int d\boldsymbol{r}\,\rho_c(\boldsymbol{r})\Psi_{\text{OCP}}^{\text{exc}}(T, \rho_c(\boldsymbol{r})). \quad (17)$$

In Eq. (17), $\Psi_{\text{OCP}}^{\text{exc}}$ denotes the reduced excess free energy per ion of a homogeneous fluid of point ions in neutralizing, uniform background which is known from Monte-Carlo simulations of the bulk plasma. Using a Car–Parrinello method, a computer simulation was performed by Löwen et al. [2] and the macroionic correlations were obtained for different parameters in the salt-free case [2] as well as in the case of added salt [4]. This calculation is called "ab initio" simulation since it takes into account counterion correlations explicitly.

An even better approximation would a weighted-density approximation for the counterion plasma [1]. This, however, has not yet been implemented as a computer simulation.

2.4. Optimal effective pair-potential

During an "ab initio" simulation, one may store typical macroion positions and the associated many-body forces induced by nonlinear counterion screening. It is tempting to fit these many-body forces by a pair potential. The potential which represents then the best fit is the optimal pair potential for the description of the macroion forces. Interestingly enough, it was found [4] that this optimal pair potential is very close to a Yukawa potential. If one discusses macroionic pair correlations (e.g. the liquid structure factor) the

optimal pair potential is sufficient as a model for the effective macroion interactions. Hence, the Yukawa potential is justified on the basis of the primitive model. It has to be noticed, however, that the amplitude and the screening constant entering into the optimal potential differ in general from their DLVO expressions (16) and (14). They also depend on the thermodynamic phase, i.e. they are different in the solid and in the fluid phase.

3. Crystallization transition in charged colloidal suspensions

3.1. Computer simulation

Once the validity of an effective screened Coulomb or Yukawa pair interaction is guaranteed by the "ab initio" simulations one may ask how the freezing transition looks like for such an interaction. For fixed Yukawa interaction and varying density and temperature, this question was answered by extensive computer simulation by Robbins and coworkers [5] and later on by Meijer and Frenkel [6]. It turns out that the system freezes into a BCC crystal if the interaction is soft and into an FCC crystal for harder interactions. Here the softness of the interaction is basically measured by the exponential decay constant κ times the mean particle distance.

However, for charged colloidal suspensions, the Yukawa interaction parameters depend on the thermodynamic parameters and also on the phase itself. One may surmise that this induces an important shift in the fluid–solid coexistence line. This problem requires detailed future studies.

3.2. Phenomenological criteria

Empirical criteria for freezing and melting are highly desirable since they permit a quick and simple estimation of the freezing parameters. The first phenomenological melting rule was proposed by Lindemann in 1910 [7]. It states that a solid melts if the ratio L of its root-mean-square-displacement and the average interparticle distance equals 0.1. This number is not completely universal; it may vary between 0.05 and 0.2 for different real and model systems [1].

Another sharp criterion of freezing was formulated in 1969 by Hansen and Verlet [8]. They found that the first maximum of the liquid structure factor has a constant amplitude of ≈ 2.85 along the freezing line.

A third criterion concerns a dynamical quantity: The ratio of the long-time to short-time self-diffusion coefficient in a Brownian (colloidal) fluid equals 0.1 along the fluid freezing line. This criterion was found recently by Löwen et al. [9] using Brownian dynamics computer simulations for Yukawa fluids as well as forced-Rayleigh scattering experiments on charge-stabilized colloidal suspensions. Also first attempts for a theoretical explanation have been published [10, 11].

3.3. Crystallization in two spatial dimensions

Since the famous works of Kosterlitz and Thoules [12], Halperin and Nelson [13] and Young [14] (KTHNY), it is known that freezing in two spatial dimensions may be fundamentally different from the usual bulk freezing in three dimensions. In particular, 2d-freezing may be a two-stage process of continuous phase transitions with an intermediate hexatic phase possessing long-ranged orientational order which contrasts to the first-order freezing transition in three dimensions.

Computer simulations, however, reveal a rather puzzling structure [15]: there is at present no evidence for a hexatic phase for hard discs [16], but for softer interaction there are strong indications for an intermediate hexatic phase [17, 18].

Looking for simple phenomenological freezing rule in two dimensions, the Lindemann rule fails since the mean-square displacement in a two-dimensional crystal is infinite. Also the Hansen–Verlet rule is not fulfilled in two dimensions. The dynamical freezing rule, however, seems to be persistent also in two dimensions. For different soft-sphere systems in two dimensions it was shown [19] that the ratio of the long-time to short-time self-diffusion coefficient is close to 0.1 near freezing. Hence it is close to its three-dimensional counterpart and the dynamical freezing is the only criterion which is valid both in two and three dimensions.

4. Two interesting open questions

It would be interesting to investigate the interactions and the phase diagram for charged colloidal confined between charged plates. In principle an "ab initio" simulation is possible including many-body forces as well as the periodic image-charges. An optimal effective pair-potential may then be derived in an analogous way as described in Section 2.4. It is quite expected that the resulting optimal pair potential is again close to a Yukawa potential. In this case it would be very interesting to simulate the full phase-diagram of the 2d Yukawa system [20] particularly focussing on the hexatic phase. First attempts have been done by Naidoo and Schnittker [21]. The motivation in studying such a confined fluid is mainly stimulated by a direct comparison of the theoretical predictions with video-image experiments [22, 23].

Another interesting problem concerns the freezing transition in a system confined between two parallel plates admitting also two or more layers. There are quite interesting different crystalline phases conceivable as a function of the distance between the plates and the particle density. It would be very interesting to calculate the corresponding phase diagram, e.g., of a hard-sphere system confined between two parallel hard plates by theory or computer simulation. First results have already been obtained [24].

Acknowledgements

My interest in charged colloidal suspensions was mainly stimulated by Jean Pierre Hansen. Furthermore, I have benefitted from discussions with Paul Madden, Thomas Palberg, Rudolf Klein, Herbert Wagner and Jean-Louis Barrat.

References

[1] H. Löwen, Phys. Reports, 237 (1994) 249.
[2] H. Löwen, P.A. Madden and J.P. Hansen, Phys. Rev. Lett. 68 (1992) 1081; H. Löwen. J.P. Hansen and P.A. Madden, J. Chem. Phys. 98 (1993) 3275.
[3] M. Fushiki, J. Chem. Phys. 97 (1992) 6700.
[4] H. Löwen and G. Kramposthuber, Europhys. Lett. 23 (1993) 673.
[5] M.O. Robbins, K. Kremer and G.S. Grest, J. Chem. Phys. 88 (1988) 286.
[6] E.J. Meijer and D. Frenkel, J. Chem. Phys. 94 (1991) 2269.
[7] F.A. Lindemann, Phys. Zeitschr. 11 (1910) 609; see also A.R. Ubbelohde, The Molten State of Matter (Wiley, Chicester, 1978).
[8] J.P. Hansen and L. Verlet, Phys. Rev. 184 (1969) 151.
[9] H. Löwen, T. Palberg and R. Simon, Phys. Rev. Lett. 70 (1993) 1557.
[10] A.V. Indrani and S. Ramaswamy, Phys. Rev. Lett. 73 (1994) 360; Phys. Rev. Lett. 74 (1995) 1491.
[11] M. Fuchs, Phys. Rev. Lett. 74 (1995) 1490.
[12] J.M. Kosterlitz and J.D. Thouless, J. Phys. C 6 (1973) 1181.
[13] B.I. Halperin and D.R. Nelson, Phys. Rev. Lett. 41 (1978) 121; D.R. Nelson and B.I. Halperin, Phys. Rev. B 19 (1979) 2457.
[14] A.P. Young, Phys. Rev. B 19 (1979) 1855.
[15] K.J. Strandburg, Rev. Mod. Phys. 60 (1988) 161.
[16] H. Weber and D. Marx, Europhys. Lett. 27 (1994) 593; H. Weber, D. Marx and K. Binder, Phys. Rev. B, 51 (1995) 14 636.
[17] K. Chen, T. Kaplan and M. Mostoller, Phys. Rev. Lett. 74 (1995) 4019.
[18] K. Bagachi et al., Phys. Rev. Lett. 76 (1996) 255.
[19] H. Löwen, Phys. Rev. E 53 (1996) R29.
[20] H. Löwen, J. Phys. Condensed Matter 4 (1992) 10 105; 5 (1993) 2649.
[21] K.J. Naidoo and J. Schnitker, J. Chem. Phys. 100 (1994) 3114.
[22] C.A. Murray and D.H. van Winkle, Phys. Rev. Lett. 58 (1987) 1200; C.A. Murray and R.A. Wenk, Phys. Rev. Lett. 62 (1989) 1643; C.A. Murray, W.O. Sprenger and R.A. Wenk, Phys. Rev. B 42 (1990) 688.
[23] D.G. Grier and C.A. Murray, J. Chem. Phys. 100 (1994) 9088.
[24] M. Schmidt and H. Löwen, Phys. Rev. Lett. 76 (1996) 4552.