Critical behavior of effective potentials in colloidal suspensions within the charged hard-sphere model

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Abstract

An effective potential for a three-component charged hard-spheres mixture is studied. The critical behavior of the effective potential, which is interpreted as ordering tendency, is discussed. Obtained results are applied to making estimates for the lattice parameters of the polysterene–water suspension. Qualitative agreement of theoretically predicted lattice parameters with the experimental values is demonstrated.

Keywords: Colloidal suspensions; Effective potential; Crystallization

1. The study of critical phenomena (short ordering, crystallization, melting) in concentrated colloidal suspensions is an important problem of liquid matter physics [1–10]. Such colloidal systems demonstrate interesting properties, in particular increasing of intensity of hydrodynamic interaction at the generation of the ordered phase [11]. On the other hand, crystal structures recently observed in colloidal suspensions and colloidal (dusty) plasmas [9, 12] give an excellent opportunity for a direct comparison between classical statistical mechanics and experiments.

Here we apply the charged hard-sphere model for the description of a colloidal suspension. A model approach to the calculation of the binary distribution functions and the static structure factors is proposed. It is related to the qualitative estimates of the effective potentials in the system under consideration which could be compared with the data for structure factors extracted from the results of neutron, X-Ray, electron-, or light-scattering experiments [1, 13, 14]. Within the framework of the proposed approach a simple analysis of the colloidal particle ordering is performed.

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2. Let us consider a water suspension of polystyrene colloidal particles (with a size of the order of $a \sim$ 0.1 μm. We note that in recent experiments [9] the crystallic phase formed by colloidal particles with the lattice constant $R_0 \sim 1$ μm could be generated.

In the following, we shall suppose that the system under consideration can be described as a three-component mixture consisting of charged hard-spheres (colloidal polystyrene particles and counter ions) and neutral hard spheres with given dipole moments (solvent molecules). The condition of the electroneutrality of the whole system is assumed to be satisfied.

In the equilibrium state the problem of the calculation of the static correlation functions $G^{\sigma\sigma'}(R_1, R_2) = F_2^{\sigma\sigma'}(R, R') - 1$ ($F_2^{\sigma\sigma'}(R, R')$ is the binary distribution function) is reduced to the determination of the effective potentials for particles of species σ and σ' located at the points R_1 and R_2, respectively,

$$F_2^{\sigma\sigma'}(R_1, R_2) = e^{-V_{\text{eff}}^{\sigma\sigma'}(R_1, R_2)/T}, \tag{1}$$

where T is the absolute temperature in energy units. Henceforth, subscript σ denotes neutral solvent

molecules ($\sigma = 1$), microions ($\sigma = 2$) and colloidal particles ($\sigma = 3$).

Static structure factors can be defined by the relations

$$S^{\sigma\sigma'}(\mathbf{k}) = \delta_{\sigma\sigma'} + \sqrt{n_\sigma n_{\sigma'}} \int d\mathbf{R} e^{-i\mathbf{k}\mathbf{R}}[e^{-V_{\text{eff}}^{\sigma\sigma'}(\mathbf{R})/T} - 1], \tag{2}$$

where $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$, n_σ is the number density of particles species σ.

The description of the system under consideration may be done on the basis of various approaches (see, for example, Refs. [15–20] and references cited therein). Here, we derive, the equation for $V_{\text{eff}}^{\sigma\sigma'}(\mathbf{R}_1, \mathbf{R}_2)$ on the basis of the well-known Ornstein–Zernike equation, which is often used for the description of critical phenomena [15, 17, 18]

$$G^{\sigma\sigma'}(\mathbf{R}_1, \mathbf{R}_2) = C_2^{\sigma\sigma'}(\mathbf{R}_1, \mathbf{R}_2)$$
$$+ \sum_{\sigma''} n_{\sigma''} \int d\mathbf{R}_3 C_2^{\sigma\sigma''}(\mathbf{R}_1, \mathbf{R}_3) G^{\sigma''\sigma'}(\mathbf{R}_3, \mathbf{R}_2), \tag{3}$$

where $C_2^{\sigma\sigma'}(\mathbf{R}_1, \mathbf{R}_2)$ is the direct correlation function. Using the hyperchain approximation [18, 19]

$$V_{\text{eff}}^{\sigma\sigma'}(\mathbf{R}_1, \mathbf{R}_2) = V^{\sigma\sigma'}(\mathbf{R}_1, \mathbf{R}_2) - \sum_{\sigma''} n_{\sigma''} T \int d\mathbf{R}_3$$
$$\left(e^{-V_{\text{eff}}^{\sigma\sigma''}(\mathbf{R}_1, \mathbf{R}_3)/T} - 1 + \frac{1}{T} V_{\text{eff}}^{\sigma\sigma''}(\mathbf{R}_1, \mathbf{R}_3) \right.$$
$$\left. - \frac{1}{T} V^{\sigma\sigma''}(\mathbf{R}_1, \mathbf{R}_3) \right) (e^{-V_{\text{eff}}^{\sigma''\sigma'}(\mathbf{R}_3, \mathbf{R}_2)/T} - 1), \tag{4}$$

where $V^{\sigma\sigma'}(\mathbf{R})$ is the direct pair potential.

We assume that $V^{\sigma\sigma'}(\mathbf{R})$ and $V_{\text{eff}}^{\sigma\sigma'}(\mathbf{R})$ can be divided into a universal short-range part $V_0^{\sigma\sigma'}(\mathbf{R})$ and long-range parts $v^{\sigma\sigma'}(\mathbf{R})$ and $\tilde{V}^{\sigma\sigma'}(\mathbf{R})$, respectively, according to

$$V^{\sigma\sigma'}(\mathbf{R}) = V_0^{\sigma\sigma'}(\mathbf{R}) + v^{\sigma\sigma'}(\mathbf{R}),$$
$$V_{\text{eff}}^{\sigma\sigma'}(\mathbf{R}) = V_0^{\sigma\sigma'}(\mathbf{R}) + \tilde{V}^{\sigma\sigma'}(\mathbf{R}), \tag{5}$$

where

$$V_0^{\sigma\sigma'}(\mathbf{R}) = \begin{cases} \infty, & R < a_{\sigma\sigma'}; \\ 0, & R > a_{\sigma\sigma'}; \end{cases} \tag{6}$$

and $a_{\sigma\sigma'} = a_\sigma + a_{\sigma'}$, a_σ being the radius of the solid core for the particles of species σ. It should be noticed,

that the hypernetted chain approximation may limit the applicability of the present theory to phase transitions. However, other approximations lead to quite similar results [23].

Substituting Eq. (5) into Eq. (4), one obtains the equation

$$\tilde{V}^{\sigma\sigma'}(\mathbf{R}) = v^{\sigma\sigma'}(\mathbf{R}) - \sum_{\sigma''} n_{\sigma''} T \int d\mathbf{R}' \left[\left(e^{-\tilde{V}^{\sigma\sigma''}(\mathbf{R}')/T} \right. \right.$$
$$\left. + \frac{1}{T} \tilde{V}^{\sigma\sigma''}(\mathbf{R}') - \frac{1}{T} v^{\sigma\sigma''}(\mathbf{R}') \right) \theta(R' - a_{\sigma\sigma''}) - 1 \right]$$
$$\times [\theta(|\mathbf{R} - \mathbf{R}'| - a_{\sigma''\sigma'}) e^{-\tilde{V}^{\sigma''\sigma'}(\mathbf{R}-\mathbf{R}')/T} - 1], \tag{7}$$

which is valid only at $R > a_{\sigma''}$.

Linearizing Eq. (7) with respect to $\tilde{V}^{\sigma\sigma'}/T$ we find the equation describing the behavior of the effective potentials far from the critical point

$$\tilde{V}^{\sigma\sigma'}(\mathbf{R}) = v^{\sigma\sigma'}(\mathbf{R}) - \sum_{\sigma''} n_{\sigma''} T \int d\mathbf{R}' \left[\theta(a_{\sigma\sigma''} - R') \right.$$
$$\left. + \frac{1}{T} v^{\sigma\sigma''}(\mathbf{R}') \theta(R' - a_{\sigma\sigma''}) \right] [\theta(a_{\sigma''\sigma'} - |\mathbf{R} - \mathbf{R}'|)$$
$$+ \frac{1}{T} \tilde{V}_{\sigma''\sigma'}(\mathbf{R} - \mathbf{R}') \theta(|\mathbf{R} - \mathbf{R}'| - a_{\sigma''\sigma'})],$$
$$R > a_{\sigma\sigma'}. \tag{8}$$

We assume that this equation can be applied to study the possibility of the *phase transition* [21, 22]. It should be realized that the linearization is not meant to describe quantitatively correct properties of effective potentials, but to lead only, on basis of singularities, to indications of conditions for ordering.

Eq. (8) can be solved by the Fourier method. It is possible to show that the Fourier representation of Eq. (8) may be written as

$$\tilde{V}^{\sigma\sigma'} + \sum_{\sigma''} \Lambda^{\sigma\sigma''}(\mathbf{k}) \tilde{V}_{\mathbf{k}}^{\sigma''\sigma'}$$
$$= \delta_{\sigma\sigma'} - T \sum_{\sigma''} n_{\sigma''} \Lambda^{\sigma\sigma''}(\mathbf{k}) \theta_{\mathbf{k}}^{\sigma''\sigma'}. \tag{9}$$

Here

$$\tilde{V}_{\mathbf{k}}^{\sigma\sigma'} = \int_{R > a_{\sigma\sigma'}} d\mathbf{R} e^{-i\mathbf{k}\mathbf{R}} \tilde{V}^{\sigma\sigma'}(\mathbf{R}),$$

$$v_{\mathbf{k}}^{\sigma\sigma'} = \int_{R > a_{\sigma\sigma'}} d\mathbf{R} e^{-i\mathbf{k}\mathbf{R}} v^{\sigma\sigma'}(\mathbf{R}),$$

$$\Lambda^{\sigma\sigma'}(\mathbf{k}) = \theta_k^{\sigma\sigma'} + \frac{1}{T}v_k^{\sigma\sigma'},$$

$$\theta_k^{\sigma\sigma'} = \int_{R>a_{\sigma\sigma'}} \mathrm{d}\mathbf{R} e^{-ikR}$$

$$= \frac{4\pi}{k^3}(\sin ka_{\sigma\sigma'} - ka_{\sigma\sigma'}\cos ka_{\sigma\sigma'}).$$

The formal solution of Eq. (9) is the following:

$$\tilde{V}_k^{\sigma\sigma'} = \frac{T}{n_{\sigma'}}(\delta_{\sigma\sigma'} - n_{\sigma'}\theta_k^{\sigma\sigma'}) - \frac{T}{n_{\sigma'}}\Pi_{\sigma\sigma'}^{-1}(\mathbf{k}), \qquad (10)$$

where

$$\Pi_{\sigma\sigma'}(\mathbf{k}) = \delta_{\sigma\sigma'} + n_{\sigma'}\Lambda^{\sigma\sigma'}(\mathbf{k}).$$

Accordingly, for the structure factor $S^{\sigma\sigma'}(\mathbf{k})$, we have

$$S^{\sigma\sigma'}(\mathbf{k}) = \sqrt{\frac{n_\sigma}{n_{\sigma'}}}\,\Pi_{\sigma\sigma'}^{-1}(\mathbf{k}).$$

Now, let us specify the long-range part of the interaction potentials for the system under consideration. For charged particles ($\sigma, \sigma' = 2, 3$), we have

$$v_k^{\sigma\sigma'} = 4\pi z_\sigma z_{\sigma'} e^2 \frac{\cos ka_{\sigma\sigma'}}{k^2}, \qquad (11)$$

where z_σ is the charge number of particles of species σ ($z_1 = 0$, $z_2 = -z_3 n_3/n_2$, z_3 is the charge number of the colloidal particles).

As regards the long-range interaction potentials between the charged particles and solvent molecules, as well as the one between the molecules, they are equal to zero in the case of nonpolar solvent, i.e. $v_k^{\sigma 1} = v_k^{1\sigma} = 0$ at $\sigma = 1, 2, 3$, and Eqs. (10), (11) give the formal solution of the problem.

If the neutral molecules have nonzero dipole moment, $\mathbf{d}$, both effective and pair interaction potentials depend on the dipole orientations and the above relations should be modified. Here, we consider two approaches to the solution of this problem. The first one consists of the assumption that orientations of the dipoles contributing to the effective potentials are strongly correlated. It means that as a first step, one can calculate the effective potentials for the given dipole orientation on basis of Eq. (10) with the following Fourier components of the long- range part of the pair

interaction potentials

$$v_k^{1\sigma} = -\frac{4\pi}{k^2}z_\sigma e i\mathbf{k}\mathbf{d}\cos ka_{1\sigma}, \quad \sigma = 2, 3,$$

$$v_k^{\sigma 1} = -v_k^{1\sigma}, \quad \sigma = 2, 3,$$

$$v_k^{11} = \frac{4\pi}{k^2} = (\mathbf{k}\mathbf{d})^2 \cos ka_{11}$$

and then perform the averaging over orientation of dipoles. The result is

$$\tilde{V}_k^{\sigma\sigma'} = \frac{T}{n_{\sigma'}}(\delta_{\sigma\sigma'} - n_{\sigma'}\theta_k^{\sigma\sigma'}) - \frac{T}{n_{\sigma'}}\langle\Pi_{\sigma\sigma'}^{-1}\rangle, \qquad (12)$$

where

$$\langle\Pi_{\sigma\sigma'}^{-1}\rangle = \frac{1}{\pi}\int_0^\pi \sin v\,\mathrm{d}v\, \Pi_{\sigma\sigma'}^{-1}(\mathbf{k},\mathbf{k}\mathbf{d})\bigg|_{kd=kd\cos v}.$$

With the approximation $\langle\Lambda^{\sigma\sigma'}\Lambda^{\sigma'\sigma_1}\tilde{V}_k^{\sigma_1\sigma'}\rangle = \langle\Lambda^{\sigma\sigma'}\Lambda^{\sigma'\sigma_1}\rangle\tilde{V}_k^{\sigma_1\sigma'}$, Eq. (12) reduces to

$$\tilde{V}_k^{\sigma\sigma'} = \frac{T}{n_{\sigma'}}(\delta_{\sigma\sigma'} - n_{\sigma'}\theta_k^{\sigma\sigma'}) - \frac{T}{n_{\sigma'}}\frac{\langle\pi_{\sigma\sigma'}\rangle}{\langle D(\mathbf{k})\rangle}, \qquad (13)$$

where $D(\mathbf{k})$ is the determinant of the matrix $\Pi_{\sigma\sigma'}$, $\pi_{\sigma\sigma'}$ is the cofactor to the matrix element $\Pi_{\sigma\sigma'}$. After the angular averaging we are led to the following expressions:

$$\langle D(\mathbf{k})\rangle = (1 + n_1\langle\Lambda_{11}\rangle)[(1 + n_2\Lambda_{22})(1 + n_3\Lambda_{33})$$
$$- n_2 n_3 \Lambda_{23}\Lambda_{32}] + n_1 n_2 n_3[\Lambda_{23}\langle\Lambda_{12}\Lambda_{31}\rangle$$
$$+ \Lambda_{32}\langle\Lambda_{21}\Lambda_{13}\rangle] - n_1 n_3(1 + n_2\Lambda_{22})\langle\Lambda_{13}\Lambda_{31}\rangle$$
$$- n_1 n_2(1 + n_3\Lambda_{33})\langle\Lambda_{21}\Lambda_{12}\rangle, \qquad (14)$$

$$\langle\pi_{11}\rangle = (1 + n_2\Lambda_{22})(1 + n_3\Lambda_{33}) - n_2 n_3\Lambda_{32}\Lambda_{23},$$
$$\langle\pi_{12}\rangle = n_1 n_3\langle\Lambda_{23}\Lambda_{31}\rangle - n_1(1 + n_3\Lambda_{33})\langle\Lambda_{21}\rangle,$$
$$\langle\pi_{21}\rangle = n_2 n_3\langle\Lambda_{13}\Lambda_{32}\rangle - n_2(1 + n_3\Lambda_{33})\langle\Lambda_{12}\rangle,$$
$$\langle\pi_{13}\rangle = n_1 n_2\Lambda_{32}\langle\Lambda_{21}\rangle - n_1(1 + n_2\Lambda_{22})\langle\Lambda_{31}\rangle,$$
$$\langle\pi_{22}\rangle = (1 + n_1\langle\Lambda_{11}\rangle)(1 + n_3\Lambda_{33} - n_1 n_3\langle\Lambda_{13}\Lambda_{31}\rangle,$$
$$\langle\pi_{23}\rangle = n_2(1 + n_1\langle\Lambda_{11}\rangle)\Lambda_{32} - n_1 n_2\langle\Lambda_{12}\rangle\Lambda_{32},$$
$$\langle\pi_{31}\rangle = n_2 n_3\Lambda_{23}\langle\Lambda_{12}\rangle - n_3\Lambda_{23}(1 + n_2\Lambda_{22}),$$
$$\langle\pi_{32}\rangle = n_1 n_3\langle\Lambda_{13}\Lambda_{21}\rangle - n_2\Lambda_{32}(1 + n_1\langle\Lambda_{11}\rangle),$$
$$\langle\pi_{33}\rangle = (1 + n_1\langle\Lambda_{11}\rangle)(1 + n_2\Lambda_{22}) - n_1 n_3\langle\Lambda_{21}\Lambda_{13}\rangle.$$

Here

$$n_1\langle\Lambda_{11}\rangle = n_1\theta_k^{11} + 4\pi\kappa\cos 2a_1;$$
$$n_1 n_{\sigma'}\langle\Lambda_{1\sigma}\Lambda_{\sigma'1}\rangle = n_1 n_{\sigma'}\theta_k^{1\sigma}\theta_k^{\sigma'1} + \frac{n_{\sigma'}}{T}v_k^{\sigma\sigma'}$$
$$\times 4\pi\kappa\frac{\cos ka_{1\sigma}\cos ka_{1\sigma'}}{\cos ka_{\sigma\sigma'}}, \quad \sigma, \sigma' = 2, 3,$$

$\kappa = n_1 d^2/3T$ is the long-range asymptotic of the polarizability of solvent.

The second approach to the problem of effective potentials in the system with polar solvent molecules consists in the generalization of the basic equations (1)–(8) to the case of potentials dependent on the orientational variables. Introducing the binary distribution functions and the relevant effective potentials $V_{\text{eff}}^{\sigma 1}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2)$ and $V_{\text{eff}}^{11}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2)$ for ion–dipole and dipole–dipole interaction, it is natural to use the following generalization of Eq. (4):

$$
V_{\text{eff}}^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2) = V^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2)
$$
$$
- \sum_{\sigma''} n_{\sigma''} T \int d\boldsymbol{R}_3 \int \frac{d\Omega_3}{4\pi}
$$
$$
\left[e^{-V_{\text{eff}}^{\sigma\sigma''}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_3, \boldsymbol{d}_3)/T} - 1 + \frac{1}{T} V_{\text{eff}}^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_3, \boldsymbol{d}_3) \right.
$$
$$
\left. - \frac{1}{T} V^{\sigma\sigma''}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_3, \boldsymbol{d}_3) \right]
$$
$$
\times \left[e^{-V_{\text{eff}}^{\sigma''\sigma'}(\boldsymbol{R}_3, \boldsymbol{d}_3; \boldsymbol{R}_2, \boldsymbol{d}_2)/T} - 1 \right], \quad \sigma, \sigma' = 1, 2, 3.
$$
(15)

In the notation used above, $V_{\text{eff}}^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2)$ and $V^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2)$ do not depend on $\boldsymbol{d}_1$ or (and) $\boldsymbol{d}_2$ at σ, or (and) $\sigma' \neq 1$; $d\Omega = \sin v \, dv \, d\varphi$, v and φ are the angles giving the direction of dipole, $V^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2)$ is the pair interaction potential. Representing the potentials for a homogeneous medium in the following form:

$$
V^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2) \equiv V^{\sigma\sigma'}(\boldsymbol{R}_1 - \boldsymbol{R}_2; \boldsymbol{d}_1, \boldsymbol{d}_2)
$$
$$
= V_0^{\sigma\sigma'}(\boldsymbol{R}_1 - \boldsymbol{R}_2) + v^{\sigma\sigma'}(\boldsymbol{R} - \boldsymbol{R}_2; \boldsymbol{d}_1, \boldsymbol{d}_2),
$$
$$
V_{\text{eff}}^{\sigma\sigma'}(\boldsymbol{R}_1, \boldsymbol{d}_1; \boldsymbol{R}_2, \boldsymbol{d}_2) \equiv V_{\text{eff}}^{\sigma\sigma'}(\boldsymbol{R}_1 - \boldsymbol{R}_2; \boldsymbol{d}_1, \boldsymbol{d}_2)
$$
$$
= V_0^{\sigma\sigma'}(\boldsymbol{R}_1 - \boldsymbol{R}_2) + \tilde{V}^{\sigma\sigma'}(\boldsymbol{R}_1 - \boldsymbol{R}_2; \boldsymbol{d}_1, \boldsymbol{d}_2),
$$

where $V_0^{\sigma\sigma'}(\boldsymbol{R})$ is defined by Eq. (6) and linearizing Eq. (15) with respect to $\tilde{V}_{\text{eff}}^{\sigma\sigma}/T$ and $V^{\sigma\sigma'}/T$, we obtain the following $\boldsymbol{k}$-representation of the linearized Eq. (15)

$$
\tilde{V}_k^{\sigma\sigma'}(\boldsymbol{d}, \boldsymbol{d}') + \sum_{\sigma''} n_{\sigma''} \int \frac{d\Omega''}{4\pi} \left[\theta_k^{\sigma\sigma''} + \frac{v_k^{\sigma\sigma''}(\boldsymbol{d}, \boldsymbol{d}'')}{T} \right]
$$
$$
\times \tilde{V}_k^{\sigma''\sigma'}(\boldsymbol{d}'', \boldsymbol{d}')
$$
$$
= v_k^{\sigma\sigma'}(\boldsymbol{d}, \boldsymbol{d}') - T \sum_{\sigma''} n_{\sigma''} \int \frac{d\Omega''}{4\pi}
$$

$$
\times \left[\theta_k^{\sigma\sigma''} + \frac{v_k^{\sigma\sigma''}(\boldsymbol{d}, \boldsymbol{d}'')}{T} \right] \theta_k^{\sigma''\sigma'},
$$
(16)

where

$$
v_k^{\sigma\sigma'}(\boldsymbol{d}, \boldsymbol{d}') = \tilde{v}_k^{\sigma\sigma'} \eta_\sigma^*(\boldsymbol{d}) \eta_{\sigma'}(\boldsymbol{d}'),
$$
$$
\tilde{v}_k^{\sigma\sigma'} = \frac{4\pi}{k^2} z_\sigma z_{\sigma'} e^2 \cos k a_{\sigma\sigma'},
$$
(17)
$$
\eta_\sigma(\boldsymbol{d}) = \begin{cases} i\boldsymbol{k}\boldsymbol{d}/z_m e, & \sigma = 1, \\ 1, & \sigma = 2, 3, \end{cases}
$$
$$
z_\sigma = \begin{cases} z_m, & \sigma = 1, \\ z_\sigma, & \sigma = 2, 3, \end{cases}
$$

z_m is the effective charge number of the particles involved in the dipole.

Using the above representation for pair potentials, Eq. (16) may be reduced to

$$
\tilde{V}_k^{\sigma\sigma'}(\boldsymbol{d}, \boldsymbol{d}') + \sum_{\sigma''} n_{\sigma''} \int \frac{d\Omega''}{4\pi} \tilde{V}_k^{\sigma''\sigma'}(\boldsymbol{d}'', \boldsymbol{d}') \theta_k^{\sigma''\sigma'}
$$
$$
+ \sum_{\sigma''} n_{\sigma''} \tilde{v}_k^{\sigma\sigma''} \eta_\sigma^*(\boldsymbol{d}) \int \frac{d\Omega''}{4\pi} \tilde{V}_k^{\sigma''\sigma'}(\boldsymbol{d}'', \boldsymbol{d}') \eta_{\sigma''}(\boldsymbol{d}'')
$$
$$
= \tilde{v}_k^{\sigma\sigma'} \eta_\sigma^*(\boldsymbol{d}) \eta_{\sigma'}(\boldsymbol{d}')
$$
$$
- T \sum_{\sigma''} \eta_{\sigma''} \theta_k^{\sigma''\sigma'} \left[\theta_k^{\sigma\sigma''} + \frac{\tilde{v}_k^{\sigma\sigma''}}{T} \eta_\sigma^*(\boldsymbol{d}) (1 - \delta_{\sigma'1}) \right].
$$
(18)

On basis of this equation, it is possible to show that the averaged values of the effective potentials

$$
\tilde{V}_k^{\sigma\sigma'} = \int \frac{d\Omega}{4\pi} \int \frac{d\Omega'}{4\pi} \tilde{V}_k^{\sigma\sigma'}(\boldsymbol{d}, \boldsymbol{d}')
$$

are given by

$$
\tilde{V}_k^{\sigma\sigma'} = \frac{T}{n_{\sigma'}} (\delta_{\sigma\sigma'} - n_{\sigma'} \theta_k^{\sigma\sigma'}) - \frac{T}{\eta_{\sigma'}} \tilde{\Pi}_{\sigma\sigma'}^{-1}(k),
$$
(19)

where

$$
\tilde{\Pi}_{\sigma\sigma'}(k) = \delta_{\sigma\sigma'} + n_{\sigma'} \left[\theta_k^{\sigma\sigma'} + \frac{\omega_k^{\sigma\sigma'}}{T} \right],
$$
(20)
$$
\omega_k^{\sigma\sigma'} = \frac{4\pi}{k^2} \tilde{z}_\sigma \tilde{z}_{\sigma'} e^2 \cos k a_{\sigma\sigma'}
$$
$$
\times \left[1 - \frac{4\pi\kappa}{\varepsilon_0(k)} \frac{\cos k a_{\sigma'} \cos k a_{\sigma''}}{\cos k a_{\sigma\sigma'}} \right],
$$
$$
\varepsilon_0(\boldsymbol{k}) = 1 + 4\pi\kappa \cos k a_{11}.
$$

Here $\tilde{z}_\sigma$ is defined by the relation

$$\tilde{z}_\sigma = \begin{cases} 0, & \sigma = 1, \\ z_\sigma, & \sigma = 3,2. \end{cases} \tag{21}$$

Comparing Eqs. (19)–(21) with Eqs. (10), (11), we see that the presence of dipole moments leads to a specific renormalization of the pair electrostatic interaction between the charged particles. Namely,

$$V_k^{\sigma\sigma'} = \frac{4\pi}{k^2} z_\sigma z_{\sigma'} e^2 \cos ka_{\sigma\sigma'} \rightarrow \omega_k^{\sigma\sigma'}$$

$$= \frac{4\pi}{k^2 \tilde{\varepsilon}_0^{\sigma\sigma'}(k)} z_\sigma z_{\sigma'} e^2 \cos ka_{\sigma\sigma'},$$

where

$$\tilde{\varepsilon}_0^{\sigma\sigma'}(k)$$

$$= \frac{\varepsilon_0(k)\cos ka_{\sigma\sigma'}}{\varepsilon_0(k)\cos ka_{\sigma\sigma'} - 4\pi\kappa \cos ka_{\sigma 1} \cos ka_{\sigma' 1}}. \tag{22}$$

Notice that the long-wave limit of the "effective dielectric permittivity matrix" $\tilde{\varepsilon}_0^{\sigma\sigma'}(k)$ coincides with the dielectric constant of the solvent

$$\lim_{k\to 0} \tilde{\varepsilon}_0^{\sigma\sigma'}(k) = 1 + 4\pi\kappa \equiv \varepsilon_0.$$

It shows that the use of ε_0 for the description of polar properties of the solvent can be an appropriate approximation only at $ka_{\sigma\sigma'} \ll 1$. Since in the case of colloidal suspensions this condition can be violated, it is better to use the general expression for "effective dielectric permittivity" (22).

As follows from the solutions for the effective potentials (10), (13) and (19), singularities of the k – representation of these potentials are defined by the secular equations

$$D(k) = \det \Pi_{\sigma\sigma'}(k) = 0, \tag{23}$$

$$\langle D(k)\rangle = 0, \tag{24}$$

and

$$\tilde{D}(k) = \det \tilde{\Pi}_{\sigma\sigma'}^{-1}(k) = 0, \tag{25}$$

respectively. These singularities determine the spatial dependence of the effective potentials. For example,

in the case of nonpolar solvents

$$\tilde{V}^{\sigma\sigma'}(R) \simeq \frac{T}{4\pi R} \sum_{k_r} \sum_{\sigma''} \frac{\pi_{\sigma\sigma''}(k)\Lambda^{\sigma''\sigma'}(k)}{\partial D(k)/\partial k} k e^{ikR} + \text{c.c.}, \tag{26}$$

where $\sum_{k_r}$ implies that the summation over the solutions of Eq. (23) at $\text{Re}\, k_r \geqslant 0$, $\text{Im}\, k_r \geqslant 0$. Similar representations describe the effective potentials also in the case of polar solvents.

If Eqs. (23)–(25) have only imaginary solutions, Eq. (26) (or, similar equations for the case of polar solvents) describe exponentially decreasing potentials. On the other hand, appearance of real roots of Eqs. (23)–(25) leads to oscillating behavior of the effective potential, which may be interpreted as a tendency to spatial ordering in the system.

It is interesting to compare the results obtained with those related to another model for effective potentials following from Kirkwood's theory [21–23]:

$$V_{\text{eff}}^{\sigma\sigma'}(R_1, R_2) = V^{\sigma\sigma'}(R_1, R_2)$$

$$- \sum_{\sigma''} n_{\sigma''} \int dR_3 V^{\sigma\sigma''}(R_1, R_3)$$

$$\times e^{-V_{\text{eff}}^{\sigma\sigma''}(R_1,R_3)/T} [e^{-V_{\text{eff}}^{\sigma''\sigma'}(R_3,R_2)/T} - 1]. \tag{27}$$

As is easy to see, in this case the relations (10), (19) remain still valid if one takes $\theta_k^{\sigma\sigma'} = 0$. Notice, that within the framework of this model in the case of Coulombic long-range potentials, Eq. (10), as well as secular equation (23) are reduced to the ones derived by Hastings [22].

3. Let us consider the secular equations (23)–(25) in more detail. For example, in the case of polar solvents with strongly correlated dipoles (which seems to be reasonable for water solutions), Eq. (24) can be rewritten in the following dimensionless form:

$$9\alpha^2 q \left\{ \varepsilon \left[\left(8\Delta(2\zeta) + \frac{\Gamma}{\zeta^2}\cos 2\zeta \right) \left(\eta_{22}^3 \Delta(\zeta\eta_{22}) \right. \right. \right.$$

$$+ \frac{\Gamma}{q^2\zeta^2}\cos(\zeta\eta_{22}) \right) - \left(\eta_{23}^3 \Delta(\zeta\eta_{23}) \right.$$

$$\left. \left. - \frac{\Gamma}{q\zeta^2}\cos(\zeta\eta_{23}) \right)^2 \right] + 2\beta \left(\eta_{23}^3 \Delta(\zeta\eta_{23}) \right.$$

$$\left. - \frac{\Gamma}{q\zeta^2}\cos(\zeta\eta_{23}) \right) \left(3\eta_{13}^3 \eta_{12}^3 \Delta(\zeta\eta_{13})\Delta(\zeta\eta_{12}) \right.$$

$$-\frac{\Gamma}{q\zeta^2\beta}4\pi\kappa\cos(\zeta\eta_{13})\cos(\zeta\eta_{12})\Big)$$

$$-\beta\left(\eta_{22}^3\varDelta(\zeta\eta_{22})+\frac{\Gamma}{q^2\zeta^2}\cos(\zeta\eta_{22})\right)$$

$$\times\left(3\eta_{13}^6\varDelta^2(\zeta\eta_{13})+\frac{\Gamma}{\zeta^2\beta}4\pi\kappa\cos^2(\zeta\eta_{13})\right)$$

$$-\beta\left(8\varDelta(2\zeta)+\frac{\Gamma}{\zeta^2}\cos 2\zeta\right)$$

$$\times\left(3\eta_{12}^6\varDelta^2(\eta_{12})+\frac{\Gamma}{q^2\zeta^2\beta}4\pi\kappa\cos(\zeta\eta_{12})\right)\Big\}$$

$$+3\alpha\left\{\varepsilon\left[8\varDelta(2\zeta)+\frac{\Gamma}{\zeta^2}\cos 2\zeta+q\left(\eta_{22}^3\varDelta(\zeta\eta_{22})\right.\right.\right.$$

$$\left.\left.+\frac{\Gamma}{q^2\zeta^2}\cos(\zeta\eta_{22})\right)\right]-\beta\left(3\eta_{13}^6\varDelta^2(\zeta\eta_{13})\right.$$

$$\left.+\frac{\Gamma}{\zeta^2\beta}4\pi\kappa\cos^2(\zeta\eta_{13})\right)-\beta q\left(3\eta_{12}^6\varDelta^2(\zeta\eta_{12})\right.$$

$$\left.\left.+\frac{\Gamma}{q^2\zeta^2\beta}4\pi\kappa\cos^2(\zeta\eta_{12})\right)\right\}+\varepsilon=0,\qquad(28)$$

where

$$\zeta=ka_3,\qquad a=n_3\Omega,$$

$$\beta=n_1\Omega,\qquad \Omega=\frac{4\pi}{3}a_3^3,\qquad \Gamma=\frac{e^2z_3^2}{Ta_3},$$

$$q=\left|\frac{z_3}{z_2}\right|=\frac{n_2}{n_3},\qquad \eta_{\sigma\sigma'}=\frac{a_\sigma+a_{\sigma'}}{a_3},$$

$$\varDelta(\zeta)=\frac{\sin\zeta-\zeta\cos\zeta}{\zeta^3},$$

$$\varepsilon=1+3\beta\eta_{11}\varDelta(\zeta\eta_{11})+4\pi\kappa\cos(\zeta\eta_{11}).$$

In the case of sizeless counter ions and solvent molecules ($a_2=a_1=0$) this equation can be transformed to

$$\left(1+\frac{3\alpha\tilde{\Gamma}}{q\zeta^2}\right)\left(1+24\alpha\varDelta(2\zeta)\right.$$

$$+\frac{3\alpha\tilde{\Gamma}}{\zeta^2}\left(\cos 2\zeta-4\pi\kappa\sin^2\zeta\right)-9\alpha\beta\varDelta^2(\zeta)\Big)$$

$$-9\alpha^2 q\left(\varDelta(\zeta)-\frac{\tilde{\Gamma}}{q\zeta^2}\cos\zeta\right)^2+9\varDelta^2(\zeta)\alpha\beta\frac{4\pi\kappa}{\varepsilon_0}=0.$$

$$(29)$$

Here $\tilde{\Gamma}=\Gamma/\varepsilon_0$. $\varepsilon_0=1+4\pi\kappa$.

In the domain of small ζ Eq. (29) has the solution

$$\zeta^2=3\alpha\Gamma\left[1+2\alpha+\frac{1}{q}(1+8\alpha-\alpha\beta)-\frac{3\alpha}{q}\tilde{\Gamma}\varepsilon_0\right]$$

$$\times\left\{\frac{\alpha\beta}{\varepsilon_0}-1-8\alpha+q\alpha^2\right.$$

$$+3\alpha\tilde{\Gamma}\left[1+\frac{\alpha}{5}\left(6+\frac{1}{q}(16-\beta)\right)+\varepsilon_0\right]$$

$$\left.-\frac{3\alpha^2\tilde{\Gamma}^2}{q}\varepsilon_0\right\}^{-1}.$$

Putting

$$a_3=0\left(\alpha\to 0,\zeta\to 0,\alpha\tilde{\Gamma}/\zeta^2=\frac{4\pi}{3}\frac{e^2z_3^2n_3}{k^2\varepsilon_0 T}\right)$$

in Eq. (29), one can find the well-known dispersion relation for an ideal plasma,

$$1+\frac{4\pi e^2z_3^2n_3}{k^2\varepsilon_0 T}+\frac{4\pi e^2z_2^2n_2}{k^2\varepsilon_0 T}=0.$$

The same result follows from Eq. (25) for the conditions mentioned above.

If the colloidal particles are neutral and counter ions are absent, Eq. (29) is reduced to

$$1+24\alpha\varDelta(2\zeta)-9\alpha\beta\varDelta^2(\zeta)/\varepsilon_0=0.\qquad(30)$$

For small values of ζ, Eq. (30) has the solution

$$\zeta^2\simeq -5\frac{1+8\alpha-\alpha\beta/\varepsilon_0}{\alpha(\beta/\varepsilon_0-16)}.\qquad(31)$$

In the case of interest ($n_1\gg n_3$, $\beta\gg 1$, $\alpha\ll 1$)

$$\zeta^2=-5\left(\frac{\varepsilon_0}{\alpha\beta}-1\right).$$

If $n_3\Omega<\varepsilon_0/(n_1\Omega-8\varepsilon_0)$, Eq. (30) has imaginary roots that corresponds to Yukawa-type effective potential. At $n_3\Omega=\varepsilon_0/(n_1\Omega-8\varepsilon_0)$ the obtained solution indicates the possibility of "soft" critical mode generation,

$$\tilde{V}_k^{\sigma\sigma'}\sim\frac{1}{k^2}.$$

This gives rise to a long-range (Colomb-like) contribution to the effective potential. With increasing $n_3\Omega$, roots of Eq. (30) become real and oscillations of the effective potential can appear.

On the other hand, taking the limit $n_1 \Omega \to 0$ in Eq. (29) or Eq. (25) at $a_1 = a_2 = 0$ (i.e. considering the two-component system consisting of colloidal particles and sizeless counter ions) we are led to the equation

$$\left(1 + \frac{3\alpha\tilde{\Gamma}}{q\zeta^2}\right)\left(1 + 24\alpha\Delta(2\zeta) + \frac{3\alpha\tilde{\Gamma}}{\zeta^2}\cos 2\zeta\right)$$
$$-9\alpha^2 q\left(\Delta(\zeta) - \frac{1}{q}\frac{\tilde{\Gamma}^2\cos^2\zeta}{\zeta^2}\right) = 0. \tag{32}$$

As mentioned above, taking formally $\Delta(2\zeta) = \Delta(\zeta) = 0$ and $a_1 = a_2 = 0$ in Eq. (25), it is possible to reproduce the secular equation derived by Hastings [22]

$$\left(1 + \frac{3\alpha\tilde{\Gamma}}{q\zeta^2}\right)\left(1 + \frac{3\alpha\tilde{\Gamma}}{\zeta^2}\cos 2\zeta\right)$$
$$-\frac{9\alpha^2\tilde{\Gamma}^2\cos^2\zeta}{q\zeta^4} = 0, \tag{33}$$

which in the case of the single-component model is reduced to

$$1 + \frac{3\alpha\tilde{\Gamma}}{\zeta^2}\cos 2\zeta = 0. \tag{34}$$

It was shown in Ref. [22] that Eq. (34) has the real root $2\zeta = 2.46$ at the minimum value of the quantity $(2\sqrt{3\alpha\Gamma})_{min} \equiv (2\kappa\alpha)_{min} = 2.79$. With increasing $\alpha\Gamma$, the value of real root of Eq. (34) decreases, however, its value cannot be less than $\zeta_{min} = \pi/4 \simeq 0.8$.

Assuming that the appearance of real roots of Eqs. (23)–(25), (32)–(34) may be interpreted as a tendency to ordering of the system, we may estimate the lattice parameter

$$R_0 = \frac{2\pi}{k} = \frac{2\pi a_3}{\zeta},$$

so that $a/R_0 \sim 0.2$ at $\zeta = 1.43$, or $a/R_0 \sim 0.13$ at $\zeta_{min} \simeq \pi/4$.

These estimates differ from the experimental results $a/R_0 \simeq 10^{-2}$ [9, 12]. Therefore, let us consider Eqs. (24), (25), (32), (33) taking into account the presence of counter ions and water molecules. These equations could not be solved analytically. The results of their numerical solution at given β and various value of q which are of our interest are presented in Figs. 1–5.

Fig. 1 shows the dependence $\alpha(\zeta)$ in the case of the two-component model calculated within the framework of Kirkwood's theory (Eq. (33)). The similar dependence obtained for the three-component system consisting of finite size colloidal particles and sizeless counter ions and water molecules on basis of Eq. (29) are shown in Fig. 2. Fig. 3 is related to the solution of the general secular equation (28) describing the model with finite sizes of all particle species. Calculations have been performed for the following values of the system parameters: $T = 293$ K, $n_1 = 10^{22}$ cm^{-3}, $\varepsilon_0 = 78$, $a_3 = 5 \times 10^{-6}$ cm, $\beta = 5.2 \times 10^6$, $z_2 = 1$. Curve numbers are related to different values of q, namely: $1 - q = 100$, $2 - q = 350$, $3 - q = 680$, $4 - q = 1000$.

Figs 4 and 5 represent the solution of the secular equation (25) for the case of the three-component system within the framework of the Kirkwood's theory generalized to the case of polar solvents $(\theta_k^{\sigma\sigma'} = 0)$ and our modification $(\theta_k^{\sigma\sigma'} \neq 0)$, respectively. As is seen from the figures, the general feature of the obtained solutions is the existence of some minimum value of α at which the real solution of the relevant equation appears. This might be interpreted as an indication to spatial ordering in the system. In the case that $\bar{\zeta}$ reaches the value of the order $\bar{\zeta} = 2\pi a/\langle R\rangle$ $(\langle R\rangle = (3/4\pi n_3)^{1/3}$ is the mean distance between the colloidal particles), i.e. the ordering distance $R_0 = 2\pi/\zeta$ coincides with the distance between the particles, it is reasonable to assume that crystal-type structure can appear. Thus, the lattice parameter R_0 and the corresponding value of the colloidal particle density at given q, β may be related to the points of intersection of $\alpha(\zeta)$-curves and $\bar{\alpha}(\zeta) = (\zeta/2\pi)^3$ (dashed lines).

In the case of the two-component model such intersections take place in the domain $\zeta > 0,8$ (Fig. 1) which is almost the same as in the case of the one-component model (29). As was mentioned above, it is not in a good agreement with the observations. In fact, introducing the charge number ratio in the experiments $q \simeq 350$ [24] (this estimate is close to the one which could be obtained from the value $q = 1400$ for particles with $a = 10^{-5}$ cm [9], if we assume, that q is proportional to the particle surface) we find from Fig. 1, $\zeta = 0.82$ instead of $\zeta \simeq 0.32$ in the experiment [9].

On the contrary, using Eq. (29) we find that for $q = 350$, the solution gives $\zeta = 0.13$ (Fig. 2) which is
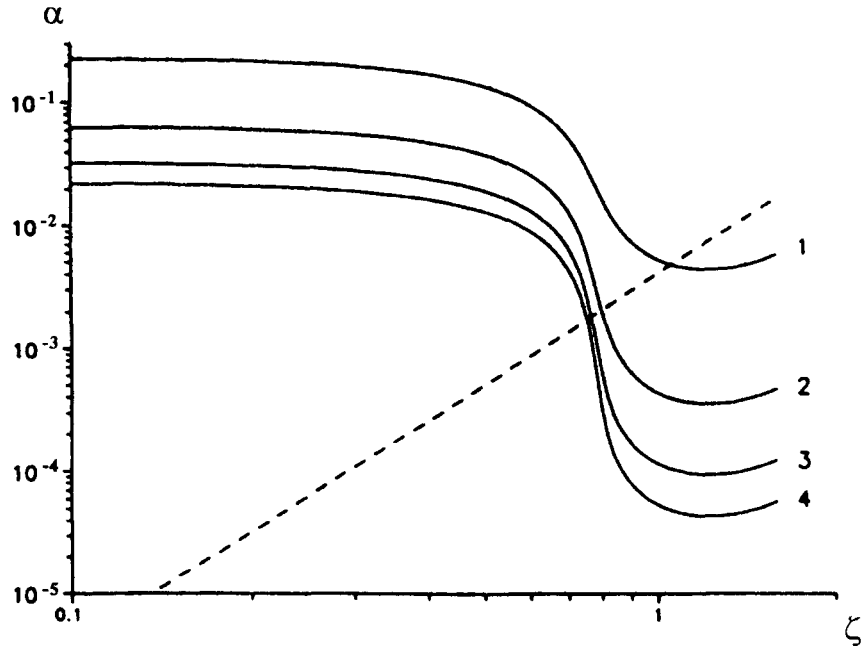
Fig. 1. Solutions of the secular equation (34) for the two-component model in Kirkwood's theory ($\Gamma_0 = e^2/a_3 T = 1.14$, $1 - q = 100$, $2 - q = 350$, $3 - q = 680$, $4 - q = 1000$; dashed line gives the dependence $\alpha(\zeta) = (\zeta/2\pi)^3$).
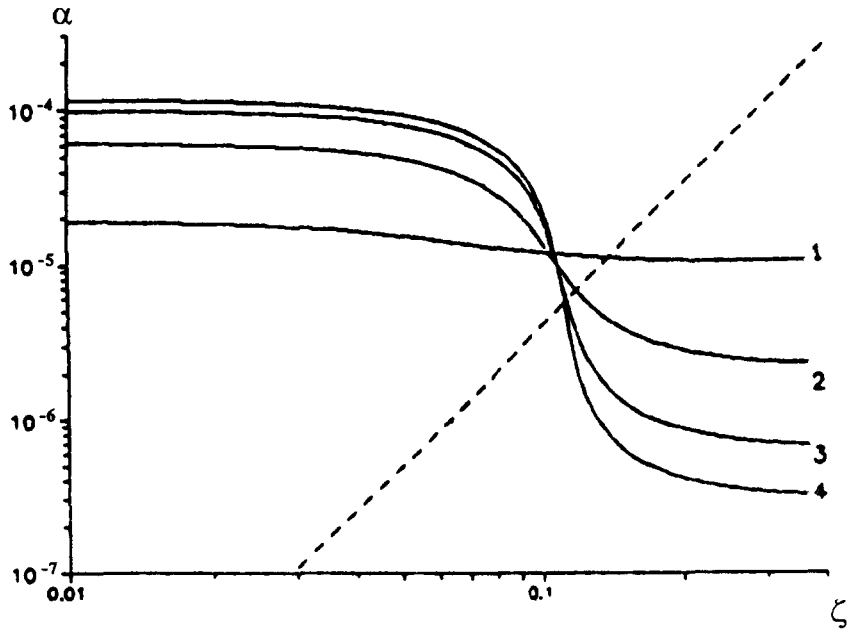

Fig. 2. Solution of the secular equation (30) for the three-component model with sizeless counter ions and water molecules ($\beta = 5 \times 10^6$, other quantities coincide with that for Fig. 1).
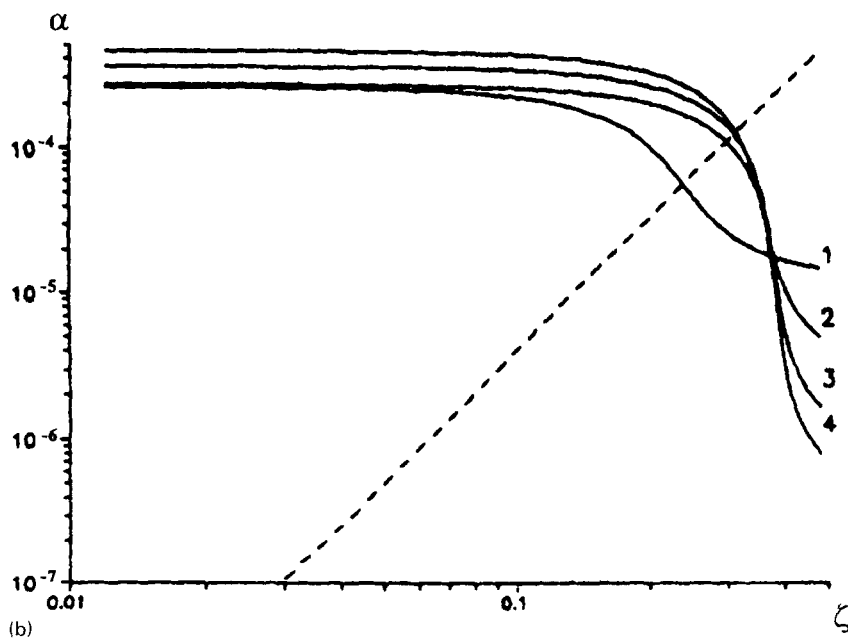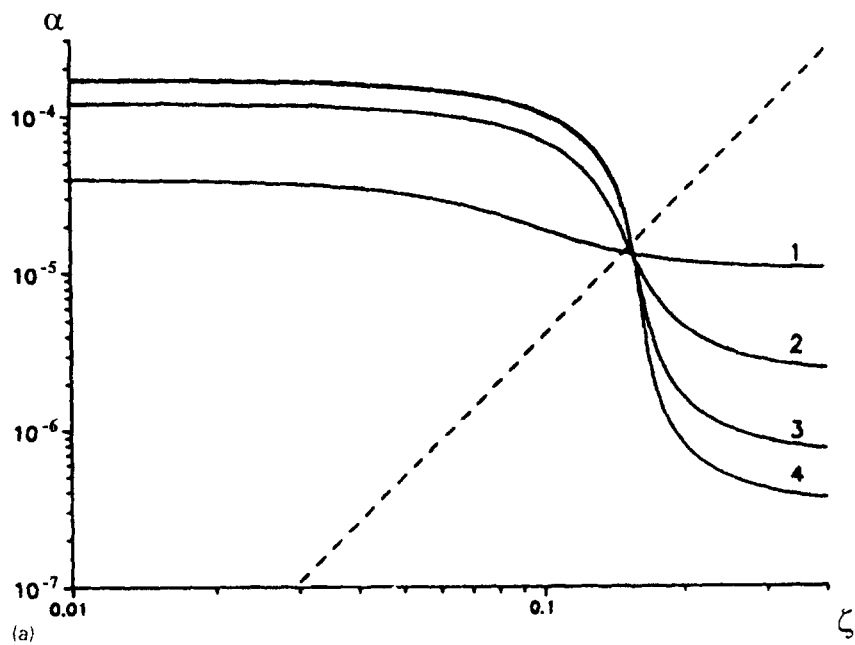
Fig. 3. Solution of the secular equation (28) for the three-component model with finite size particles of all species: (a) $a_1/a_3 = a_2/a_3 = 3 \times 10^{-3}$; (b) $a_1/a_3 = a_2/a_3 = 7 \times 10^{-3}$, other quantities coincide with that for Fig. 2.
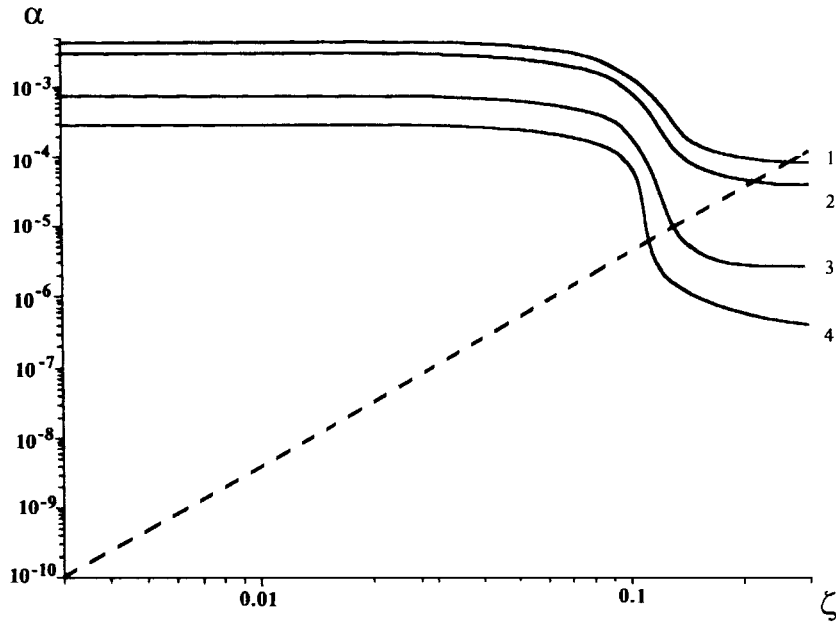
Fig. 4. Solution of the secular equation (25) for the three-component model with $\theta_k^{\sigma\sigma} = 0$ (Kirkwood's theory in the case of polar solvent) with sizeless molecules and microions ($1 - q_1 = 70$, $2 - q = 100$, $3 - q = 350$, $4 - q = 1000$).
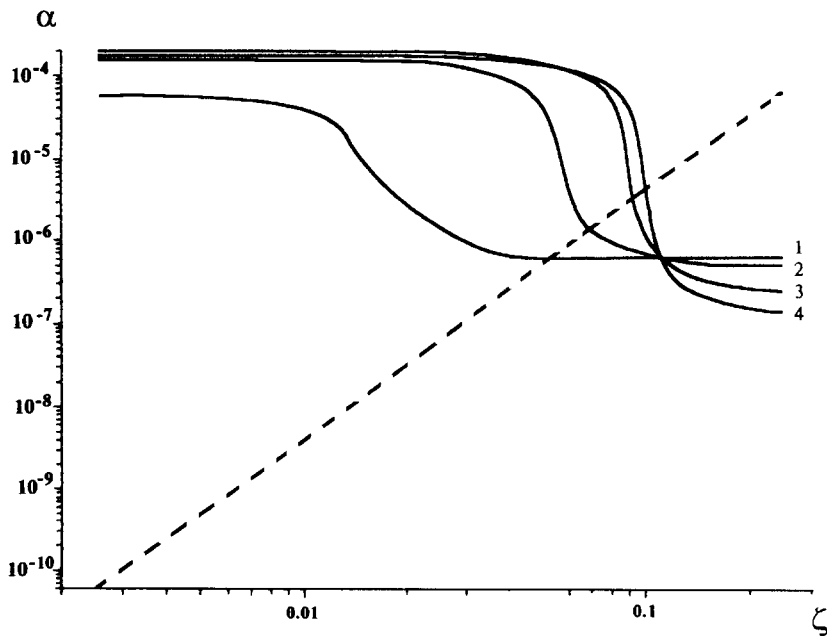

Fig. 5. Solution of the secular equation (25) for the three-component model with finite sizes of counter ions and water molecules ($1 - q = 100$, $2 - q = 350$, $3 - q = 1000$, $4 - q = 1500$, $a_1/a_3 = a_2/a_3 = 3 \times 10^{-3}$).

about two times less than the experimental value. Similar pictures are observed in the case of Kirkwood's theory for solutions with polar solvents (Fig. 4) and for the general secular equation (25) (Fig. 5).

The best agreement between theory and experiment is achieved, if we use Eq. (28) taking into account particle sizes for all species. Assuming that water molecules and counter ions $(H_3O)^+$ have sizes of the order of $a_1 = a_2 \sim 1.5$ Å we see that $\zeta = 0.16$ (Fig. 3(a)). However, since water is an associated liquid in which molecules form water dimers, it is possible to estimate $a_1 \sim a_2 \sim 3.5$ Å which leads to $\zeta \sim 0.3$ (Fig. 3(b)) in good agreement with experiment.

For particles with $a = 10^{-6}$ cm, $q = 1400$ [9] the appropriate calculations give $\zeta = 0.28$.

4. Thus, the performed analysis shows that an appropriate description of the order parameter of a colloidal suspension can be given within the framework of the three-component model involving a two-component charged hard-sphere system (colloidal particles and counter ions) and neutral hard spheres with dipole moments (water molecules) with the assumption of strong correlation of dipole orientations. The two-component model gives an estimate of a/R_0 about three times larger than the experimental value, while the three-component model with size-less counter ions and water molecules, as well as the secular equation (25), lead to a smaller value of the above ratio. Obviously, the simple model used in the present paper gives only a qualitative indication of the crystallization phenomena. However, such simplified consideration may be useful, since it provides the possibility to study the critical behavior of the binary distribution function without detailed computer experiments.

References

[1] G. Brady and J. Gravatt, J. Chem. Phys. 55 (1971) 5095.
[2] B.J. Ackerson and N.A. Clark, Phys. Rev. Lett. 46 (1981) 125.
[3] P. Pieranski, Contemp. Phys. 24 (1983) 25.
[4] P. Pieranski and P.B. Strzelecki, Phys. Rev. Lett. 50 (1983) 900.
[5] D.J.W. Aastuen, N.A. Clark and L.K. Cotter, Phys. Rev. Lett. 57 (1986) 1733.
[6] C.A. Murray and D.H. van Winkle, Phys. Rev. Lett. 58 (1987) 1200.
[7] W. Van Megen and P.N. Pusey, Phys. Rev. A 43 (1991) 5429.
[8] W. Götze and L. Sjogren, Phys. Rev. A 43 (1991) 5442.
[9] J. Derksen and W. van de Water, Phys. Rev. A 45 (1992) 5660.
[10] H. Löwen, Phys. Rep. 237 (1994) 249.
[11] Europhys Conf. Abstr. 2nd Liquid Matter Conf. 18–22 Sept, 1993, Firenze, Italy, 17 G.
[12] J.H. Chu, Lin. Physica A 205 (1994) 183.
[13] H. Temperly, J. Rowlinson and C. Rushbrooke, Physics of Simple Liquids (North-Holland, Amsterdam, 1968).
[14] E.B. Sirota, H.D. Ou-Yang and S.K. Sinha et al., Phys. Rev. Lett. 62 (1989) 1524.
[15] I.R. Yukhnovsky and M.F. Holovko, Statistical theory of Classical Equilibrium Systems Kiev, Naukova Dumka, 1980 (in Russian).
[16] J.R. Hunsen and I.R. Mc Denald, Theory of Simple Liquids (Academic Press, London, 1986).
[17] S.G. Brush, H.L. Sahlin and E.J. Teller, Chem. Phys. 45 (1966) 2022.
[18] Yu.L. Klimontovich, Statistical physics, Harwood, Chur (1986).
[19] R. Balescu, Equilibrium Statistical Mechanics.
[20] M.O. Robbins, K. Kremer and G.S.J. Grest, Chem. Phys. 88 (1988) 3286.
[21] J.G. Kirkwood, Chem. Rev. 19 (1936) 275.
[22] R.J. Hastings, Chem. Phys. 68 (1978) 675.
[23] O.I. Gerasimov, A.G. Zagorodny and Yu.L. Klimontovich, Plasma Phys. Rep. 19 (1993) 83.
[24] M. Hoppenbrouwers, private communication.