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Static and dynamic screening effects in electrostatic self-assembly of nano-particles

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In the description of charge screening in electrostatic self-assembly of nanoparticles (molecules) embedded into a polar solvent, the *static* screening effects (a contribution associated with the rapid spatial redistribution of small and highly mobile ions of a solvent) is traditionally treated phenomenologically, using the Yukawa short-range potential for describing the interaction between these particles. However, this model has a limited range of applicability being valid only for infinitely diluted systems and high salt concentrations. During a slow self-assembling process with nanoparticle formation, very dense structural elements (aggregates) are formed, in which the distances between the nanoparticles could become to be comparable to the Debye radius in the Yukawa potential. For such the structural elements *dynamic* screening effects (the contribution of nanoparticles themselves into the screening potential) becomes important. In this paper, using a novel integrated approach (nonlinear integro-differential kinetic equations for the correlation functions of particles), we have obtained the self-consistent solution in 3d case and compare roles of both static (equilibrium) and dynamic (nonequilibrium) charge screening effects in different situations. This paper is a continuation of our recent study [Phys.Chem.Chem.Phys., 16, 13974 (2014)], where the polar solvent effects now were taken into account.

1 Introduction

This is a second part of the study of nonequilibrium charge screening for systems with self-assembly in 3d case. The first part of the study was published recently in Ref.[1].

As is well known, nanoparticles (NPs) of different materials could be functionalized with charged ligands[2] and used as building blocks in producing ordered structures[3,4] in nanoscale *self-assembly* (SA). However, an important problem of the interaction of the charged NPs embedded into the salt solution (polar solvent) remains unsolved. This is largely due to the fact that the outcome seems obvious: salt ions are expected to redistribute around the NPs so that the long-range Coulomb potential becomes strongly screened and effectively turnes out to be a short-range[5,6]. But, as always, the devil is in the details. The generally-accepted model of the interaction of charged particles embedded in saline is known as the Yukawa potential[2,6], $\phi(r) \propto \exp(-\kappa r)/r$. This potential is characterized by a single parameter κ (inverse of the Debye radius[2,6], $r_D = \kappa^{-1}$). Since this radius is determined entirely by parameters of salt solution, it is not difficult to evaluate it as a function of salt concentration. It is evident that the change in salt concentration changes also the interaction potentials between NPs, and, as a result, it is possible to observe the SA-related phase transitions induced by a salt. This is indeed confirmed experimentally: inorganic salts determine the SA of charged NPs in a form of different composite structures[7], for example, the charged NPs nucleate and grow into all-NP crystals at negligible or low salt concentrations, but they start to form supraspheres at higher salt concentrations. Within the traditional approach, in general, the process in different salt solutions with a fixed value r_D must lead to the same structures. However, this is not the case. Instead, the experiments show that different salts with the same Debye screening length r_D reveal $different$ structures[7]. This fact indicates that the simple theoretical scheme based on the systematic use of the Yukawa potential is unsatisfactory, at least for describing the SA processes.

As is well known, the Yukawa potential is not an exact result, but quite a rough approximation (the so-called *linearized* Poisson-Boltzmann equation[2,6]). Moreover, it completely neglects the short-range particle interactions. Therefore, a more advanced approach is needed for analysis of the NPs interaction with small electrolyte ions[8]. The outcome could be a revised expression for the interaction potentials of NPs correcting the standard Yukawa potential.

This idea has been implemented recently in the approach[8] combining both analytical calculations and computer simulations. The screened Coulomb interactions between spherical charged NPs immersed in a simple electrolyte was calculated and several effective parameters (screening length, renormal-

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ized charges, etc) were found. This approach, however, is not universal. The interactions between NPs were determined from simulations with two macroions (NPs) in an ensemble of small ions which corresponds to infinitely small densities of NPs. Note that this limiting case coincides with the range of applicability of the Yukawa potential[9]. However, this limit is completely incompatible with the SA objectives. In fact, typical elements of SA structures are very dense aggregates or clusters. At some stage of SA process, the distances between NPs become of the order of the screening length r_D. For such dense systems the contribution the NPs to the screening effects can be significant. In other words, both the traditional method (a single-parameter Yukawa model[2]), and a more elaborated approach[8] are not designed for the SA tasks.

The reason for this is obvious: the consideration of static and dynamic effects in the charge screening effects is performed in the very different ways. The screening effects occur as a result of the regrouping of all charges, both the solvent ions and NPs, nearby a probe particle. The existing theory considers, however, only *static* effect caused by a rapid regrouping of small solvent ions (quasi-equilibration). Despite the fact that as a result of such the rearrangement a local structure is formed, wherein each charge effectively surrounded by a cloud of particles of opposite charge, small solvent ions are distributed macroscopically essentially uniformly. Therefore, a concentration of the salt in solution is an important parameter determining the screening effects. On the other hand, completely different behavior is observed for slow NPs (*dynamic* screening effects).

As a result of SA process, even in the systems with a low concentration of NPs, they can form very dense aggregates. The density of NPs determines primarily a number of aggregates, but not their characteristics. The structural elements of the NP system have a local density comparable to the density of a solid. As a result, the dynamic screening effects could be large under all conditions, which may cause SA. Moreover, they may be more significant than the traditionally considered static screening effects. This effect is not associated with electrostatics and is quite general[10]: a strong interaction between particles with irreversible aggregation is a diffusion-limited process (a purely kinetic phenomenon that results in the structures even at arbitrarily low particle volume fraction. Of course, systems with weaker attractions require larger volume fractions for SA.

Note some additional restrictions. In computer simulations (kinetic Monte Carlo - kMC, or Molecular dynamics, MD)[9,11] the assumption of moderate or high salt concentration (large values of parameter κ) is commonly used. This restriction arises for the two reasons. One reason is trivial and purely technical. A system with a small κ (or even with zero $\kappa = 0$ in absence of salt) is almost impossible to simulate by means of traditional methods (kMC), because the interaction radius r_D is so large that each NP interacts with a large number of other NPs caught in the sphere of its influence. Another reason is more fundamental: use of the Yukawa potential assumes neglect of solvent-induced fluctuations[11]. This limitation is important for the case of the static screening effect. In the case of electrostatic SA, taking into account the dynamic screening effects, the aggregates are always dense and full charge density fluctuations are suppressed. Moreover, SA is characterized by a fundamentally different spectrum of fluctuations, with strongly developed long-range correlations, responsible for the aggregation[1].

The general problem of NPs screening has been formulated by us recently[1,12–14], but it was not solved properly: we took into account the dynamics screening effects but neglected the static effects. This is valid only for absence of salt solution (formally, $\kappa \equiv 0$). Note that this case is almost impossible to simulate by conventional methods (for example, kMC) because of the infinite range of the interaction of particles. Therefore, in Refs.[1,12–14] the new approach was formulated, the basic ideas of which are listed below, Section2.1. The kinetics in two-dimensional (2d)[12–14] and three-dimensional (3d)[1] systems of NPs were considered in detail.

In this paper, we first consider the screening of the charges in a competitive static and dynamic effects. We consider realistic 3d case, so for better understand of the results, it is desirable prior acquaintance with the recent study[1].

We use essentially the same model for electrostatic dynamic SA as in previous Refs.[1,12–16] taking into account the competition of long-range, Section 2.2, and short-range, Section 2.3 particle interactions. Despite the simplicity of the model, it successfully describes a system with different *kinetic phase transitions*, and therefore is ideal for demonstration of the dynamic screening effects in electrostatics.

2 Model and methods

2.1 Smoluchowski-type equations

It is well know, that the formal solution of stochastic equation of Brownian dynamics for *a single* particle in the external field $U(\mathbf{r})$ leads to the Fokker-Planck equation[17] for the conditional probability of time evolution (famous Smoluchowski equation):

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = D\nabla[\nabla c(\mathbf{r},t) + \frac{c(\mathbf{r},t)}{k_B T}\nabla U(\mathbf{r})], \qquad (1)$$

where $c(\mathbf{r},t)$ is the probability density to find a particle at position $\mathbf{r}$ at time t. As shown in Ref.[12] (see also Refs.[18,19] for more detail), for a system of *interacting particles* the method should be based on generalized Fokker-Planck equation. So, the complete set of kinetic equations is of the Smoluchowski-type (indexes α, β are two types of particles):

$$\frac{\partial F_{\alpha\beta}(r,t)}{\partial t} = D_{\alpha\beta}\nabla[\nabla F_{\alpha\beta} r,t) + \frac{F_{\alpha\beta}(r,t)}{k_B T}\nabla W_{\alpha\beta}(r,t)], \quad (2)$$

where $D_{\alpha\beta} = D_\alpha + D_\beta$ is the coefficient of mutual diffusion. The eq. (2) for the joint correlation functions, $F_{\alpha\beta}(r,t)$, describes the effective particle diffusion in *potentials of mean forces*, $W_{\alpha\beta}(r,t)$, that are, in its turn, functionals of the correlation functions $F_{\alpha\beta}(r,t)$ (see Appendix, section 5.1 for more details). This is typical for condensed matter self-consistent theory. The statistical meaning of the joint correlation functions is fully analogous to the *radial distribution function* in statistical physics of dense gases and liquids. The quantities

$$C_\beta^{(\alpha)}(r,t) = n_\beta F_{\alpha\beta}(r,t) \quad (3)$$

are average densities of NPs β-type at the relative distance r provided that a probe particle α is placed into the coordinate origin[18,19] and n_β are macroscopic densities of β-type NPs. The joint correlation functions are normalized to unity (no spatial correlations, random distribution of particles at long distances)

$$F_{\alpha\beta}(\infty,t) \equiv 1. \quad (4)$$

Without discussing derivation of the equation set (it was done in detail in Ref.[12]), we note only that they coincide with the first nontrivial *exact* equations based on many-body theory, very similar to the Bogolyubov - Born - Green - Kirkwood - Yvon (BBGKY) hierarchy (see also Refs.[18,19]), whereas the effective potentials of mean forces, $W_{\alpha\beta}(r,t)$, are obtained approximately[12]. Note that so-called Kirkwood approximation[20] was used for calculating the contribution of short-range interactions in the potentials of mean forces[12] (Appendix, section 5.1). The evaluation of accuracy of the Kirkwood approximation for Smoluchowski-type equations is discussed in Ref.[18,19]. The electrostatic contribution to the potentials of mean forces, will be discussed in detail below. The set of coupled kinetic non-linear and integro-differential equations (2) is solved numerically by using special numerical methods[12] (see Appendix, sections 5.2 and 5.3 for more details).

2.2 Electrostatic interactions

In our earlier work for 2d[12–14] or 3d[1] ionic systems, we considered important limiting case of the absence of salt. There the dynamic screening of the NPs occurs only as the result of particle spatial rearrangement. The starting point for the electrostatic contribution to the potentials of mean forces was the same as in the Debye-Hückel theory[2]: a continuum method for the calculation effective electrostatic potential ϕ for charged NPs in an ionic solution was used. In the absence of a salt one can use the Poisson's equation in the differential form

$$\nabla^2\phi(r,t) = -\frac{4\pi}{\varepsilon}\rho_{NP}(r,t), \quad (5)$$

where ε is a dielectric constant and $\rho_{NP}(r,t)$ the charge density of NPs (it can be the function of time in kinetic systems). This equation needs a self-consistent solution: we are looking for the electrostatic potential $\phi(r,t)$ produced by a spatial distribution of charged particles, eq.(5). The charge density ρ_{NP} can be easily related to the densities of NPs and the joint correlation functions by using the definition, eq.(3). The right hand side (rhs) of the eq.(5) is a simple linear functional of the correlation functions, $\rho_{NP} = \rho_{NP}[F(r,t)]$. But, in turn, a spatial distribution of charged particles depends on the potential, eq.(2).

Thus, the rhs of the eq.(5) is effectively a very complex functional of the electrostatic potential $\phi(r,t)$. However, for the solution of this equation the contributions of short-range interactions (avoiding the traditional catastrophe of Poisson-Boltzmann method for 3d[2]), and the effects associated with the non-equilibrium (kinetics) are important.

In the case of the salt absense, a simple two-component ($\alpha, \beta = A, B$) system was considered in Refs.[1,12–14]. It is characterized by the three *time-dependent* joint correlation functions: two for similar particles, $F_{AA}(r,t)$ and $F_{BB}(r,t)$, and one for dissimilar, $F_{AB}(r,t)$. From a formal point of view, one can suggest to include the solvent effects considering additionally two types of oppositely charged small ions in the salt.

However, with four types of particles the total number of the correlation functions reaches already 10, and this complication is not the only one. First of all, the very idea of using the Brownian dynamics for small ions is questionable. This could be justified, strictly speaking, only for NPs moving in a viscous liquid. If we assume its applicability for small ions, different types of particles will have different mobilities: slow diffusion of NPs and a rapid diffusion of small ions. Of our interest, however, is a slow dynamics of the NPs, so that fast variables should be excluded. Moreover, from a formal point of view, to solve the set of kinetic eqs.(2), the potentials of *all* interactions (NP-NP, NP-ions, ions-ions) must be specified. With the increasing number of interactions considered in the theory, the number of free parameters also increases, that hinders understanding of the physical results.

Thus, our first simplification is to *neglect* the degrees of freedom of ions in the electrolyte, and to treat it as a viscous liquid with a small number of parameter for the description of electrostatic interaction between NPs. This is very similar to the transition from Newton dynamics to Langevin (Brownian) dynamics[21]. In our case, we are interested in the time evolution of a *subset* of the degrees of freedom. These (NPs) degrees typically are collective variables changing only slowly in a comparison to other (ions in the electrolyte) variables of the system. The fast (microscopic) variables are responsible only for the static screening of charge.

As a result of eliminating redundant degrees of freedom, we return to eqs.(2) for NPs only, but with modified potentials of mean forces. We will proceed from the simple assumption that small particles do not change the short-range interactions of NPs, but they are significant for the screening their long-range interactions. Instead of the eq.(5), we have to use a more general equation

$$\nabla^2\phi(r,t) = -\frac{4\pi}{\varepsilon}[\rho_{NP}(r,t) + \rho_{salt}(r,t)]. \qquad (6)$$

Since statistical characteristics of small particles (correlation functions) are not considered, the term $\rho_{salt}(r,t)$ on the rhs of the eq.(6) (responsible for static screening effects) can only be the functional on the potential $\phi(r,t)$, $\rho_{salt}(r,t) \equiv \rho_{salt}[\phi(r,t)]$. The choice of this functional depends on the electrolyte model. The main ideas of our study will be demonstrated below for the simplest (and generally accepted) model with a linear functional of $\phi(r,t)$,

$$\frac{4\pi}{\varepsilon}\rho_{salt}[\phi(r,t)] \equiv -\kappa^2\phi(r,t), \qquad (7)$$

where salt is described by a single parameter κ. In other words, we start from the equation

$$\nabla^2\phi(r,t) - \kappa^2\phi(r,t) = -\frac{4\pi}{\varepsilon}\rho_{NP}(r,t). \qquad (8)$$

This equation is nothing else but the so-called *linearized* Poisson-Boltzmann equation[2], where, however, the statistical characteristics are used for the description of dynamic screening effects, $\rho_{NP} = \rho_{NP}[F(r,t)]$, similar to Ref.[1]. Note that in the limiting case of a very low density of NPs, for example, e.g. just one NP, $\rho_{NP}(r,t) = e_\alpha\delta(\mathbf{r})$, the solution of the eq.(8) reads

$$\phi(r,t) = e_\alpha \exp(-\kappa r)/\varepsilon r. \qquad (9)$$

In other words, in the limit of small NPs concentrations, the non-screened Coulomb potential, $\phi \propto 1/r$, is replaced by the screened (Yukawa) one, $\phi \propto Q^{DH}(r)/r$, where the screening factor $Q^{DH}(r) = \exp(-\kappa r)$ according the Debye-Hückel theory, is the function of a single parameter κ. Note that for a more complex model of salt[8] it is necessary to consider more complex functionals for $\rho_{salt}[\phi(r,t)]$ with a large number of free parameters.

The solution of the eq.(8) can always be presented in the form $\phi(r,t) \propto Q(r,t)/r$ with a simple boundary condition $Q(0,t) = 1$, where the screening factor $Q(r,t)$ is now the function of time. As shown in Ref.[1,13], the dynamic screening factor $Q(r,t)$ may have nothing to do with the equilibrium factor, $Q^{DH}(r)$. Furthermore, in the systems with asymmetrical diffusion or charge, each type of charged particles is screened differently, so that the two screening factors exist here, $Q_A(r,t)$ and $Q_B(r,t)$.

The Coulombic interaction of particles is characterized by another parameter, so-called Bjerrum length[2] (the length at which the electrostatic interaction between two charges is comparable in magnitude to the thermal energy scale, k_BT):

$$l_B = \frac{e^2}{\varepsilon k_B T}. \qquad (10)$$

This parameter characterizes the contribution of NPs to the electrostatic potential. Therefore, the interaction of NPs in different salts with the same Debye radii r_D will be different because of the difference in the Bjerrum lengths.

2.3 Short-range interactions

To simulate the short-range van der Waals interactions between oppositely charged A and B NPs, the classical 6-12 Lennard-Jones potential (with two free parameters, U_0 and r_0) is used. We assume attractions and repulsion of both similar pairs,

$$U_{AA}(r) = U_{BB}(r) = 4U_0[(\frac{r_0}{r})^{12} - (\frac{r_0}{r})^6]. \qquad (11)$$

The Lennard-Jones potential corresponds to the particle repulsion at short distances, $r < r_c = 2^{1/6}r_0$ (due to finite particle sizes). We assume a similar repulsion of dissimilar pairs of NPs at $r < r_c$ but cut the dissimilar pair attraction at $r > r_c$ (truncated and shifted, Weeks-Chandler-Andersen potential[12,15,21,22]):

$$U_{AB}(r) = 4U_0[(\frac{r_0}{r})^{12} - (\frac{r_0}{r})^6 + \frac{1}{4}] \qquad (12)$$

for $r \leq r_c = 2^{1/6}r_0$, and $U_{AB}(r) \equiv 0$ for $r > r_c$. Without Coulomb interactions dissimilar NPs, A and B, repel each other whereas similar NPs (A-A, B-B) attract each other and thus could aggregate.

2.4 Parameters

The length unit r_0 and the diffusion time unit $t_0 = r_0^2/(D_A + D_B)$ are used hereafter. The screening parameter κ and the wave number q (a definition of the structure factors $F_{\alpha\beta}(q,t)$

will be introduced below) are considered in the units of r_0^{-1}. The Coulomb potential is described by the dimensionless Bjerrum length $\zeta = l_B/r_0$ (the ratio of the unscreened Coulomb interaction energy on the characteristic length of the particle diameter r_0, $e^2/\varepsilon r_0$, to the thermal energy, k_BT). As is shown below, the nature of the screening of charged particles is primarily determined by the competition between the two parameters, κ and ζ. It is convenient also to use dimensionless temperature $\theta = k_BT/U_0$.

The NPs are assumed to have opposite charges Z: $e_A = Z_Ae$, $e_B = -Z_Be$ (the value of $Z_B = 1$ is fixed). The NPs densities are n_A and n_B, so that the total particle density, $n = n_A + n_B$, determines the dimensionless average (macroscopic) NPs concentration $\eta = nr_0^3$. Lastly, asymmetry in the particles' diffusion coefficients is described by the parameter $\mu = D_A/(D_A + D_B)$. These five parameters are of fundamental importance because they determine all macroscopic thermodynamic quantities.

2.5 Limitations of the method

The main goal of our paper was to demonstrate new type of dynamical screening effects in self-assembly systems of nanoparticles which were neglected so far. This needs calculation of the kinetics on time scales much longer than traditional MD simulations. Indeed, we consider here the results for the long simulation times, $t = 2^m$ (in units of $t_0 = r_0^2/(D_A + D_B)$), where the maximum value $m = 24$ corresponding to the dimensionless time 10^7 or real time $1 - 10$ sec. On the other hand, MD technique allows currently to reach only millisecond time scales (or $t = 10^3$ dimensionless units). In other words, our approach and MD observe quite different stages of the kinetic process.

Note that any self-consistent theory (in our case eqs.(2)) is always semi- quantitative, and its accuracy should be, in principle, estimated by a comparison with the results of independent computer simulations. In fact, we did so in our previous studies (e.g., Refs.[18,19]). However, as mentioned above, the problem is that the method developed here predict results on the time scales far exceeding the limits of standard MD and kMC methods.

The price of this achievement is use of very simplified models, focused on fundamental phenomena without details and free parameters which would complicate understanding of the results. This is a generally accepted approach in kinetic theory[1,2,9,11,12,15,16]. Thus, we used the model of structureless nanoparticles which interact only via Coulomb and short-range van der Waals-like potentials. Such simple model systems with spherically symmetric, structureless nanoparticles reveal successfully several kinetic phase transitions. These transitions are defined by parameters of particle interactions. Note that treatment of more realistic atomistic models (with ligands and their internal structure, different dielectric constants for core and the surrounding solvent) currently is hardly possible, because by the increase in the number of particle species and types of interactions results can only be obtained in the time interval that is not interesting from the point of view of the effect.

2.6 Structure characteristics

When considering the results, we use the same set of structural characteristics as used in previous studies[1,13,14]:

- Primarily, as the result of solving the set of kinetic eqs.(2) for arbitrary time t, we analyze the joint correlation functions $F_{\alpha\beta}(r,t)$. We focus on the ordering formation from chaos: random *initial* distribution of NPs is assumed, $F_{\alpha\beta}(r,0) = 1$. This distribution corresponds to a well-stirred system.

- The additional information can be obtained from the *partial structure factors* $S_{\alpha\beta}(q,t)$.

Its Faber-Ziman[23] definition is used here

$$S_{\alpha\beta}(q,t) + 1 + n\int_0^\infty [F_{\alpha\beta}(r,t) - 1]\frac{\sin(qr)}{qr}4\pi r^2 dr. \tag{13}$$

The behavior of the structure factors at small wave numbers q corresponds to the large-scale fluctuations of the particle densities.

3 Results

3.1 Absence of salt, $\kappa = 0$

In recent Ref.[1] we presented the results of a preliminary study of the important limiting case of the absence of salt between NPs. In this case one has to consider *explicitly* the contribution of the long-range interactions of a given NP with all other NPs. The screening of the NPs occurs only as the result of NPs spatial rearrangement rather from electrolyte small particles. Formally, this case corresponds to the choice of the parameter $\kappa = 0$. As we show below, the results could be successfully extrapolated to the general case of small salt concentrations. For $\kappa = 0$ the only parameter that characterizes the strength of the Coulomb interaction is ζ. Depending on its value, different types of structures could arise. Let us conditionally classify the range of values $\zeta < \zeta_0 \sim 1$ as a *weak* Coulomb interaction[1]. Within this range of the control parameter ζ the system always remains far from equilibrium: a continuous growth of aggregates occurs, from small to large ones (known as the Ostwald ripening). The value ζ_0 is critical in the sense that for $\zeta > \zeta_0$ (but not too large values, medium Coulomb interaction, $\zeta < \zeta_1 \sim 10^2$) the system rapidly reaches equilibrium corresponding to the steady state with very small aggregates. In other words, *the kinetic phase transition* occurs. With further increase of the parameter ζ, there is another kinetic phase transition for $\zeta = \zeta_1$(ionic crystallization)[1], which we do not consider in this paper.

The range of values $\zeta < \zeta_0 \sim 1$ is interesting from the point of view of a comparison of both dynamic and static screening effects. Here we have a typical dynamic SA. The structure of aggregates is complex, with characteristic charge oscillations. The kinetics of the process can be analyzed in terms of non-equilibrium physics of critical phenomena, because the long-wavelength ($q \to 0$) fluctuations of particle densities are well developed here[1], similarly to the critical point in equilibrium systems.

For weak Coulomb interactions the mutual attraction of similar particles at short distances is stronger than their Coulomb repulsion. Thus, similar particles have a trend to form dense domains. But a linear domain size λ is limited due to the Coulomb repulsion of similar particles within the domain. This length λ is a function of the parameters θ and ζ. Each domain acts as a super-particle with a big charge, Ne, at distances $r \gg \lambda$, N is a mean number of similar particles in the domain, which is large for the weak Coulomb interaction[1]. So, the effective value of the electrostatic parameter $\zeta_{eff} \sim N^2\zeta$ is not small, but big. The only important effect is the Coulomb interaction between domains, and it is strong. As a result, ionic solid-type crystallization occurs between domains of opposite charges.

3.2 Weak static screening

The results for the parameter value $\kappa = 0.5$ can be conditionally assigned to the case of a weak static screening. A comparison of Fig.1 for the case of presence of salt, $\kappa \neq 0$, with the analogous data for $\kappa = 0$ (Fig.4 in Ref.[1]) shows their similarity. There is only a small quantitative difference. The presence of salt weakens the strength of the Coulomb interaction, so the results[1] can be reproduced with appropriate increase of the parameter ζ.

Fig.1a shows the principal result: the correlation functions are not stationary, the process of structure formation continues. The results for other values of the parameter η are very similar to those shown in the Fig.1, all figures describe the same type of the structures. This behavior is typical for dynamic screening effects.

This is confirmed by a comparison of the partial structure factors, Fig.1b, where quantitative difference is not large and has kinetic nature. The aggregate formation of the same size but in a less dense medium requires more time. Note that the correlation functions $F_{\alpha\beta}(r,t)$ and partial structure factors $S_{\alpha\beta}(q,t)$ contain the same statistical information (structure factors are the result of the Fourier transform of the correlation functions, eq.(13)). However, for nonequilibrium structures studied in this work (which are not universal, but correspond to specified particle interactions) the use of structural factors is preferable, since their behavior is much simpler. Being the function of the argument q, these factors have only one or two extremes, each of which has a simple physical interpretation.

First, at long times they have maxima with close magnitudes. Moreover, it is possible to use the non-linear fit of the Lorentz type, $S(q_c)/[1+\xi^2(q-q_c)^2]$, for all factors $S_{\alpha\beta}(q,t)$ near the point $q = 0$. Both, the peak maxima at $q = q_c$ (the value q_c is small) and their half-widths increase with time. The existence of this peak for the pairs of similar particles, $S_{\alpha\alpha}(q,t)$, indicates that as the result of interactions they form aggregates (domains with similar particles).

As shown in Ref.[1], this behavior is similar to that in the equilibrium statistical systems near the *critical points* (Ornstein-Zernike theory[24,25]) in the limit $t \to \infty$ (infinitely large time). The long-wavelength part of the fluctuation spectrum, $q \to 0$, is unstable, as the result of particle aggregation.

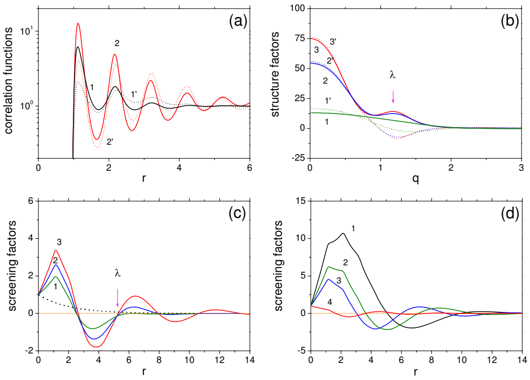

Fig. 1 (Color online) Ionic binary systems with Lennard-Jones and Coulomb interactions for fixed parameters $\kappa = 0.5$ (weak static screening) and $[\eta, \theta, \mu = 0.4, 0.5, 0.5]$. (a) The joint correlation functions $F_{\alpha\beta}(r,t)$ (solid line - similar, dotted line - dissimilar pairs, numbering with prime) for the value $\zeta = 1.0$ and times t: (1) 2^{18}, (2) 2^{24}. (b) The structure factors $S_{\alpha\beta}(q,t)$ (solid line - for similar and dotted line - for dissimilar pairs) for the same ζ and the times t: (1) 2^{18}, (2) 2^{22}, (3) 2^{24}. (c) The screening factors $Q(r,t) = Q_A(r,t) = Q_B(r,t)$ for the same times as in window (b). Note: dashed line - results according the Debye-Hückel theory, $Q^{DH}(r) = \exp(-\kappa r)$ (without dynamic screening effects). (d) The screening factors $Q(r,t)$ at time $t = 2^{24}$ and for different values of parameter ζ: (1) 0.25, (2) 0.50 (3) 0.75, (4) 2.00.

If a similar peak simultaneously occurs also for the dissimilar particles, function $S_{AB}(q,t)$, it means that in this system the charged domains serve as the building elements of heterogeneous structure where all kinds of particles (similar or dissimilar) are spatially correlated. In other words, the aggregation of homogeneous domains occurs with alternating charges forming a heterogeneous structure. Fig.1b corresponds exactly to this case. If the factor $S_{AB}(q,t)$ has no maximum but a minimum (this case is also possible, as shown in Section 3.4), it means NPs segregation.

Second, the competition of weak electrostatic and short-range interactions leads to formation of the structures with oscillating charges[12–16], because these aggregates are made of domains with different-sign charges. One can see in Fig.1b the emergence of additional extremes at $q = q_0 \approx 1$. This value may be associated with the previously mentioned characteristic length $\lambda = 2\pi/q_0$[1]. Note that this extremum arises only at very long times, curves (3), and then does not change with time.

Very interesting is the behavior of the screening factors. Difference between the results again has the kinetic nature (different rate processes in a more or less dense environments), and not very large. The results are also not very sensitive to the choice of the parameter η. For short times, when aggregates do not have enough time to form, this factor practically coincides with the equilibrium estimate $Q^{DH}(r) = \exp(-\kappa r)$ (dashed line in Fig.1c This result is expected. However, the appearance of dense aggregates leads to oscillations of the charge and results in the nontrivial dynamic screening effects (all factors show oscillations with the same period λ).

One can see that the overall behavior of the screening factors differ from the prediction of the standard Debye-Hückel theory[2]. A comparison of the results for screening factors with their counterparts for $\kappa = 0$ (absence of salt)[1] shows an additional difference. In the absence of salt a complete charge screening, $Q(\infty,t) = 0$, takes a long time necessary for the slow NPs redistribution in space on a large scale. Therefore, the asymptotic value of the screening factors $Q(\infty,t)$ may differ from zero. In the presence of salt, rapid movement of its small ions provides a rapid establishment of the asymptotic behavior, $Q(\infty,t) = 0$.

Fig.1d shows the behavior of the screening factors at the same time, but for different values of the parameter ζ (the parameter κ is fixed).

The results discussed above are very important for understanding of the relevant experiments[7]. It means that different salts with the same value of the Debye screening length $r_D = \kappa^{-1}$ but not the same value of another electrostatic parameter ζ could have different type of the screening and could produce different ordered structures. The systematic increase of parameter ζ results in decrease of both the amplitude of the oscillations and the oscillation period λ. For the value $\zeta = 2.0$ the aggregation stops, the system of charged NPs quickly relaxes to the equilibrium gas-like structure. Thus, the definition of the weak Coulomb interaction, $\zeta < \zeta_0 \sim 1$, in Ref.[1] is justified by the results of kinetics for systems with a salt contribution.

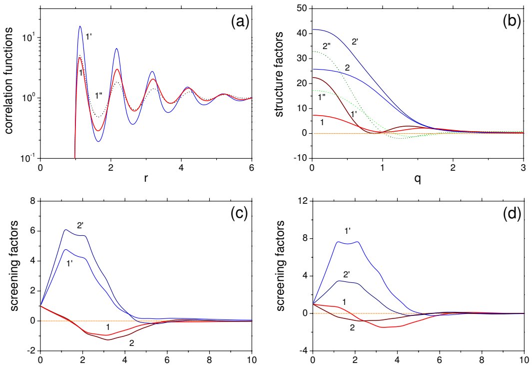

Fig. 2 (Color online) (a-c) Ionic binary systems with Lennard-Jones and Coulomb interactions for asymmetric particle charges, $Z_A = 2, Z_B = 1$, and fixed parameters $\kappa = 0.5$ (weak static screening). Parameters: $[\eta, \theta, \mu, \zeta = 0.4, 0.5, 0.5, 0.75]$. Solid line - for similar and dotted line - for dissimilar pairs. (a) shows the joint correlation functions for the time $t = 2^{24}$ (curve (1) AA, curve ($1'$) BB, and ($1''$) AB correlations). (b) the structure factors for the times t: (1) 2^{18}, (2) 2^{24}. (c) the screening factors $Q_A(r,t)$ (curves without primes) and $Q_B(r,t)$ (curves with primes) for the same times. (d) shows the screening factors at times $t = 2^{24}$ for the same parameters$[\eta, \theta, \mu = 0.4, 0.5, 0.5]$, but with two different values of ζ: (1) 0.5 and (2) 1.0.

The observed structure does not change much by varying the control parameters (provided that they meet conditions of the dynamic SA). It may be, however, changed dramatically during the transition to systems with charge asymmetry.

Fig.2 shows the results for the system, where the charge of one type of particles exceeds that of other particles: $Z_A = 2, Z_B = 1$. (We do not show qualitatively similar results for other values of the asymmetry of the charge.). Due to the electrical neutrality, we assume $n_B/n_A = Z_A/Z_B$. The relevant correlation functions become asymmetric, $F_{AA}(r,t) \neq F_{BB}(r,t)$, Fig.2a. The same is true for the structure factors $S_{AA}(q,t) \neq S_{BB}(q,t)$, Fig.2b, or the screening factors $Q_A(r,t) \neq Q_B(r,t)$, Fig.2c.

This type of structure differs considerably from the previous case of equal charges. In particular, the oscillations of the screening factor are no longer observed. However, the behavior of the screening factors still has nothing to do with the results of the Debye-Hückel theory. One may notice that different charges are screened in a qualitatively different way. It is because NPs with a larger charge, A, are isolated from each other (their number is relatively small).

As the result, they are mainly surrounded by a cloud of oppositely charged NPs, B (they are in excess). This cloud reduces rapidly the effective charge of the particle A with the increasing distance. Simultaneously, the sign of the effective charge is changing (curves (1) and (2) in Fig.2c. At the same time, the NPs B aggregate into domains. Their effective charge is determined by a number of similar particles in the domain, N. As the result, the effective charge can reach high values (overcharging, curves ($1'$) and ($2'$) in Fig.2c. Fig.2d shows the behavior of the screening factors for different values of the parameter ζ.

Summarizing this subsection, we can formulate the fundamental result. The use of the Yukawa potential is justified *only* at the initial stage of the kinetics, when the structure of the system is close to gas or liquid. But at the beginning of dynamics SA (at the first appearance of dense aggregates), such a strong dynamic screening effect occurs that makes the use of the Yukawa potential incorrect. However, there is no other universal potential for these systems. For each structure, effective interaction between the particles must be calculated separately.

3.3 Medium static screening

With further increase of the parameter κ, one gets into an area which is called medium static screening, Fig.3 for value $\kappa = 1$. A new element here is the sensitivity of the results to changes in a parameter ζ. Unlike the previous figures, the window Fig.3b does not show the time evolution of the structural factors, time is fixed. The only parameter ζ is varied here. Note that the critical value ζ_0, above which dynamic SA disappears, increases ($\zeta_0 \approx 3$). Curves (4) correspond approximately to the critical point where the solutions come to the equilibrium. Here some aggregates are formed, but they are small, as can be judged by the absence of the characteristic additional extremum at q_0. This extremum arises with decreasing ζ, curves (3), but in a very narrow range.

The process is non-stationary: the aggregates grow, gluing of homogeneous domains of the size λ. With further decrease of ζ this additional extremum of the structure factors disappears again, curves (1) and (2). This is the kinetic effect: in this range of parameter ζ very large homogeneous domains are formed that have simply not enough time to stick together into aggregates over the time interval studied. In turn, the large size of the domains is the result of a static screening. The size λ is determined by the contribution of the Coulomb repulsion of similar particles within the domain, and this repulsion is now weakened. Moreover, the stucking together of domains with different charges is suppressed, as the static screening weakens the Coulomb interaction at large distances.

These conclusions are supported by Fig.3d where the behavior of the screening factors is shown for the same ζ values. The curve (4) corresponds to a strongly screened potential, but very different from the Yukawa one. The curve (3) corresponds to aggregates with charge oscillations. The curves (1) and (2) confirm the existence of homogeneous domains (there is an excess charge), but they are not stuck together (no oscillations). Fig.3c shows the kinetics of adhesion of different-type domains: how oscillations of the screening factors are well pronounced.

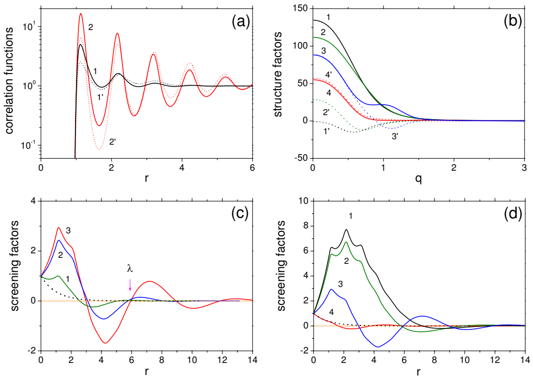

Fig. 3 (Color online) Ionic binary systems with Lennard-Jones and Coulomb interactions for fixed parameters $\kappa = 1.0$ (medium static screening) and $[\eta, \theta, \mu = 0.4, 0.5, 0.5]$. Solid line - for similar and dotted line - for dissimilar pairs. (a) shows the joint correlation functions for $\zeta = 2.0$ and times t: (1) 2^{18}, (2) 2^{24}. (b) The structure factors for the time 2^{24}. The values of parameter ζ are: (1) 0.75, (2) 1.0, (3) 2.0 and (4) 3.0. (c) The screening factors $Q(r,t) = Q_A(r,t) = Q_B(r,t)$ for for $\zeta = 2.0$ and times t: (1) 2^{18}, (2) 2^{22}, (3) 2^{24}. Note: dashed line - results according the Debye-Hückel theory, $Q^{DH}(r) = \exp(-\kappa r)$ (without dynamic screening effects). (d) The screening factors $Q(r,t)$ at time $t = 2^{24}$ for the fixed time $t = 2^{24}$. The values of parameter ζ are the same as in window (b).

We supplement the obtained results with one example for the case of charge asymmetry, $Z_A = 2, Z_B = 1$ in Fig.4. When comparing with the previous results for the weak static screening, Fig.2, it is difficult to detect qualitative differences. The quantitative differences, however, are observed, especially a strong sensitivity of the results to a small change in the parameter ζ near the critical point $\zeta_0 \approx 2$, Fig.4d (critical value varies slightly with the appearance of the charge asymmetry).

In other words, for the system with dynamic SA in this range of parameters the effects of dynamic and static screening are combined, and the contribution of *both* effects is essential. Note that in the case of the charge asymmetry the structure is more stable and does not change much by variation of the parameter κ. For this reason, in the next subsection we no longer give examples for this case.

The case considered here confirms again the absence of an universal potential (similar to the Yukawa potential), with which it would be possible to describe all the structures of SA systems. The effective interactions should be found for each specific type of structures, by solving the relevant self-consistent problem.

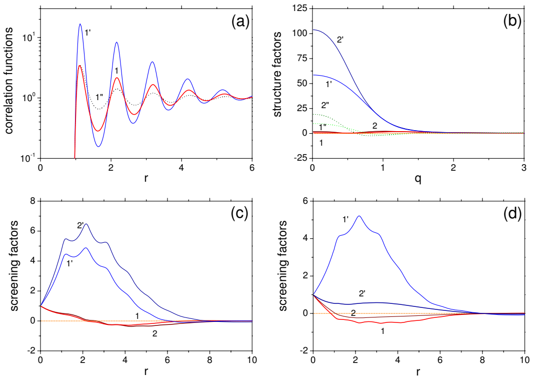

Fig. 4 (Color online) Ionic binary systems with Lennard-Jones and Coulomb interactions for asymmetric charge, $Z_A = 2, Z_B = 1$ and fixed parameters $\kappa = 1.0$ (medium static screening). Parameters: $[\eta, \theta, \mu, \zeta = 0.4, 0.6, 0.5, 0.75]$. Solid line - for similar and dotted line - for dissimilar pairs. (a) shows the joint correlation functions for the time $t = 2^{24}$ (curve (1) - AA, curve (1$'$) - BB, and (1$''$) - AB correlations). (b) The structure factors for the times t: (1) 2^{20}, (2) 2^{24}. (c) The screening factors $Q_A(r,t)$ (curves without primes) and $Q_B(r,t)$ (curves with primes) for the same times. (d) The screening factors at time $t = 2^{24}$ for the same parameters, but two different values of ζ: (1) 2.0 and (2) 2.2.

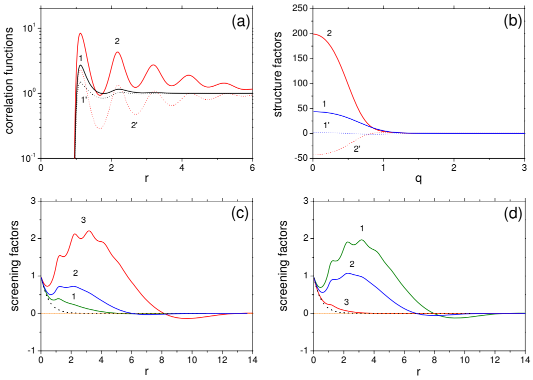

Fig. 5 (Color online) Windows (a-d): Ionic binary systems with Lennard-Jones and Coulomb interactions for fixed parameters $\kappa = 2.0$ (strong static screening) and $[\eta, \theta, \mu = 0.4, 0.7, 0.5]$. Information: solid line - for similar and dotted line - for dissimilar pars. The window (a) shows the joint correlation functions for $\zeta = 3.0$ and times t: (1) 2^{18}, (2) 2^{24}. The window (b) shows the structure factors for times: (1) 2^{22}, (2) 2^{24}. The window (c) shows the screening factors $Q(r,t) = Q_A(r,t) = Q_B(r,t)$ for the times t: (1) 2^{20}, (2) 2^{22}, (3) 2^{24}. Note: dashed line - results without salt contribution. The window (d) shows the screening factors $Q(r,t)$ at time $t = 2^{24}$. The values of parameter ζ are: (1) 3.1, (2) 3.3 and (3) 4.0.

3.4 Strong static screening

With further increase of the parameter $\kappa = 2$ (strong dynamic screening) the qualitatively different behavior is found. We specifically stipulate that all information below, as well as earlier, applies only to the case of relatively small values of the parameter $\zeta < \zeta_0$, because there a typical dynamic SA structure exists. From the Fig.5d one can see again that the small change of parameter ζ near the point $\zeta_0 \approx 4$ lead to drastic changes of the screening factor.

The curves (1) and (2) in Fig.5d indicate the existence of domain of similar particles, resulting in the effect of *overcharging* at short distances. At the same time, there are no previously observed oscillations of the structure factors. This means that domains with different charges practically do not attract each other: domains no longer stick into the aggregates. This is not surprising, since the effect of the static screening is very strong and the interaction of NPs with the chosen value of the parameter κ is practically short-range. When the electrostatic interactions are weak, the most important contribution in the short-range part of the potential is the Lennard-Jones one. For qualitative understanding, the long-range suppresed Coulomb interactions could be neglected. Since in our model similar particles attract each other whereas and dissimilar repel, only homogeneous aggregates (domains of similar particles) can grow.

At the same time, such the behavior of the screening factors is no longer observed, see curve (3), Fig.5d. Moreover, the screening factors are very close to the exponential (the dashed line), thus corresponding to the Yukawa potential. Here the formation of large domains is no longer possible, instead, the stationary distribution of small aggregates occurs, where the contribution of the dynamic screening effects is no longer important.

In areas with continuous increase of the domain size, the screening factors show no steady-state, Fig.5c. Moreover, the behavior of other structural characteristics is also not stationary: see the correlation functions, Fig.5a, and the structural factors, Fig.5b.

The behavior of the structural factors differs fundamentally from those presented earlier. In the case of the formation of aggregates with the charge oscillations, all the structural factors reveal a maximum near the point $q = 0$. Here we see, however, that only the functions $S_{\alpha\alpha}(q,t)$ for the similar particles have a maximum, whereas the function $S_{AB}(q,t)$ has a minimum. This behavior was observed earlier for a system without Coulomb interactions[1]. The effect is very simple: there is aggregation of similar particles and segregation of disimilar ones. Thus, a strong static screening virtually eliminates all effects associated with the presence of the long-range Coulomb interaction, since the pattern formation rules can be observed in the systems with purely short-range interactions. Again, we conclude that there is no universal potential for this case for a simple description of the electrostatic interactions.

4 Conclusions

In this paper, the competition between static and dynamic screening effects was investigated for electrostatic dynamic self-assembly in ionic three-dimensional systems. The static effects results from a rapid redistribution (quasi-equilibrium) of small and mobile charged ions in the electrolyte (salt) around the charged nanoparticles. Instead, the dynamic screening effects arise due to the rearrangement of large, charged and slow mobile NPs in the process of self-assembly.

During the self-assembly of nano-particles, dense structural units (aggregates) are formed, wherein the particles have a local density close to solid state. As a result, unlike the static effects, the dynamic screening effects are almost independent of the average NPs concentrations. We have shown that the traditional description of a system of charged particles, based on the use of the short-range Yukawa potential, is hardly suitable to describe the self-assembly process, but still could be used under some specific condition (high salt concentration or static self-assembly with small sizes of aggregates).

The integrated approach based on combined analytical and numerical solution of nonlinear self-consistent kinetic equations was developed and applied. This allows us to study kinetics in the complex systems with long-range interactions on the time scale exceeding many orders of magnitude what could be performed by means of commonly used kMC or MD.

A complete set of statistical characteristics of the system, including the sets of the joint correlation functions (radial distribution functions), partial structure factors, as well as the charge screening factors was obtained. The results obtained could be useful for understanding of the electrostatic dynamic self-assembly of nanoparticles and large molecules in chemistry, physics and biology.

Acknowledgments

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5 Appendix

5.1 The mean force potentials

The formally exact definition of the potentials of mean forces were discussed in our previous paper; eq.(9) in Ref.[12]. These definitions are rather cumbersome for a general case of a system containing many types of different particles, as they must take into account various combinations of pair interactions. However, the structure of equations is quite simple. The mean force acting on a particle A has both the contribution from *direct* interaction with another particle (A or B type) as well as from *indirect* interactions (integral terms). It is the latter integral terms which make numerical solution very time consuming.

For illustration, we present here only one typical indirect term, omitting details (such as indices determining the types of particle). After using the Kirkwood superposition approximation[20], we obtain a set of standard-type integrals:

$$\nabla W(r) = n \int \nabla U(r'') f(r'') g(r') d\mathbf{r}', \tag{14}$$

$$\mathbf{r}'' = \mathbf{r} - \mathbf{r}' \tag{15}$$

containing the potential $U(r)$ for short-range interaction within pairs AA, BB or AB, respectively. These potentials are defined by eqs.(11) and (12). To simplify the notations, we introduced two functions of the coordinates (time argument is omitted) $f(r)$ and $g(r)$, which are different joint correlation functions, $F_{\alpha\beta}(r,t)$. Thus, the rhs of the mean force potential definition, eq.(14), is non-linear, and this non-linearity is of the second-order (for the correlation functions). The same is true for the expression of full potentials which are sums of such the terms discussed here.

To solve the kinetic eqs.(2), we need to know only the radial part of eq.(14). After a series of analytic transformations, the problem can be reduced to the standard form:

$$\frac{\partial}{\partial r} W(r) = \pi n \int_0^\infty \frac{\partial}{\partial r'} U(r') \cdot f(r') dr' \int_{r''_{min}}^{r''_{max}} \mathscr{L}(r,r';r'') r'' dr'', \tag{16}$$

$$\mathscr{L}(r,r';r'') = g(r'') \frac{r^2 + (r')^2 - (r'')^2}{r^2}. \tag{17}$$

where

$$r''_{min} = |r - r'|, \tag{18}$$

$$r''_{max} = r + r'. \tag{19}$$

As one can see, it is necessary to calculate a set of one-dimensional integrals, where the calculation results of one of the integrals are used to calculate other integrals. After the standard discretization with coordinate increments $\triangle r$, $r_i = i\triangle r$, the integrals can be calculated by means of the standard trapezoid method. The calculation of the integral terms for short-range potentials is time-consuming since the integral kernels here depend on the correlation functions and cannot be calculated preliminary.

It should be noted that the determination of the potentials of mean forces for the Coulomb interaction is a simple task, since only differential eq.(8) is solved in radial coordinates. From the structure of eq.(8), where the rhs is the functional of the correlation functions, it is clear that the electrostatic potentials, and hence the potentials of the mean forces, are functionals of the correlation functions.

As can be seen from the above example, the potentials of mean forces are, in general, non-linear functionals of the correlation functions. Thus, a formally simple kinetic eqs.(2) are in fact strongly nonlinear, which is typical of the self-consistent theory.

Along with calculating the potentials, it is necessary to solve several other technical problems described below.

5.2 Solving of kinetic equations

The main problem arises due to the necessity of solving nonlinear, partial differential equations with singular potentials. To illustrate our method of their solution, let us consider the typical equation for 3d case

$$\partial g(r,t)/\partial t = r^{-2}\partial[r^2 j(r,t)]/\partial r, \qquad (20)$$

$$j(r,t) = \partial g(r,t)/\partial r + \partial W[g,r,t]/\partial r\, g(r,t)\ . \qquad (21)$$

Here $W[g,r,t]$ are functionals of $g(r,t)$ sought for and $W[g,r,t]$ has a singularity: $W[g,r,t] = \infty$ as $r \to 0$. After the discretization of the equation using the standard method, $r_i = i\triangle r$, $t_m = m\triangle t$, $g(r_i,t_m) = g_i^0$, $g(r_i,t_{m+1}) = g_i$, we arrive at the difference equation which could be presented in a quasi-linearized traditional tridiagonal form[26]

$$a_i[\bar{g}]g_{i-1} + b_i[\bar{g}]g_{i+1} - c_i[\bar{g}]g_i - g_i/\triangle t = -g_i^0/\triangle t\ , \qquad (22)$$

where coefficients a_i, b_i, c_i arise due to the approximation of $r^{-2}\partial[r^2 j(r,t)]/\partial r$. These coefficients depend on $W[g,r,t]$ and thus are functionals of g. Solution of eq.(22) is obtained by means of a quasi-linearization: (i) $\bar{g}_i = g_i^0$ is used as an initial guess, (ii) eq.(22) is solved in the standard way, (iii) then we substitute $\bar{g}_i = g_i$ and (iv) the iterative process continues until convergence is achieved within a requared tolerance. In this way we avoid a problem of the non-linearity of the kinetic equations.

Eq.(22) can be conveniently solved using the tridiagonal matrix algorithm (also known as the Thomas algorithm)[26]. Note that the so-called stable schemes avoid a problem of unlimited growth of errors in the numerical calculations. In particular, this algorithm will always converge if the tridiagonal system is diagonal dominant[26], that is, if

$$|c_i + 1/\triangle t| \geq |a_i| + |b_i|. \qquad (23)$$

Unfortunately, the standard approximation does not guarantee fulfillment of this condition, coefficients a_i and b_i generally do not have a definite sign and can take a very large absolute values. The reason is that potentials can change rapidly in a narrow interval of variables. Moreover, they are singular at $r \to 0$. Accordingly, the stability can only be achieved within a very small time steps, $\triangle t \to 0$. As a result, the standard methods can yield results only for a small time interval, which is unacceptable for our physical problem.

There is, however, a relatively simple method to obtain a stable scheme for diffusion problems. The idea of this method (renormalization of the diffusion equation) has been demonstrated previously for the diffusion equation in one-dimensional problem[27]. We generalized this idea for the three-dimensional systems.

5.3 Renormalization of the diffusion equation

Let us consider in detail the non-trivial expression of $r^{-2}\partial[r^2 j(r,t)]/\partial r$. The procedure is as follows. To obtain a *conservative* difference scheme, one integrates the initial differential equation in the spherical layer within the coordinate interval $r \in [r_{i-1/2}, r_{i+1/2}]$ with $r_{i\pm1/2} = (i \pm 1/2)\triangle r$. The problematic term reads now

$$\int (r^{-2}\partial[r^2 j(r,t)]/\partial r) r^2 dr = r^2_{i+1/2} j_{i+1/2} - r^2_{i-1/2} j_{i-1/2}. \qquad (24)$$

In the equation for the flux density, $j = \partial g/\partial r + (\partial W/\partial r)g$, substitution $g = \exp(-W)\omega$ gives $j = (\partial\omega/\partial r)\exp(-W)$. It is important that the exponent, $\exp(W)$, has the argument W rapidly changing on the scale of coordinate increment Δr and thus also changes rapidly as compared to the slowly varying function j[27]. This is why the integral in the interval $r \in [r_{i-1}, r_i]$

$$\int j \exp(W) dr = \omega_i - \omega_{i-1} \qquad (25)$$

could be estimated as

$$\int j \exp(W) dr \approx j_{i-1/2} \int \exp(W)\ dr \approx$$
$$\approx j_{i-1/2} \frac{\Delta r}{2}\ (\exp(W_i) + \exp(W_{i-1}))\,. \qquad (26)$$

Now returning from the intermediate function ω to g sought for, one obtains the basic relation for the difference scheme coefficients

$$j_{i-1/2} = (g_i \exp(\Delta W_i) - g_{i-1})\, \frac{2}{\triangle r} \frac{1}{\exp(\Delta W_i) + 1}, \qquad (27)$$

$$j_{i+1/2} = (g_{i+1}\exp(\Delta W_{i+1}) - g_i)\,\frac{2}{\triangle r}\,\frac{1}{\exp(\Delta W_{i+1})+1}. \quad (28)$$

where $\Delta W_i = W_i - W_{i-1}$. As it should be, the flux density depends not on the very potential W but on its derivative. The obtained approximation, eq.(26), is then used in eq.(24) to calculate the coefficients a_i, b_i, c_i in the difference scheme, eq.(22).

Here are the basic formulas:

$$a_i g_{i-1} + b_i g_{i+1} - c_i g_i = \frac{1}{v_i}\int (r^{-2}\partial[r^2 j(r,t)]/\partial r) r^2 dr, \quad (29)$$

$$v_i = \int r^2 dr = \frac{r^3_{i+1/2} - r^3_{i-1/2}}{3}. \quad (30)$$

$$a_i = \frac{r^2_{i-1/2}}{v_i \Delta r}\,\frac{2}{\exp(\Delta W_i)+1}, \quad (31)$$

$$b_i = \frac{r^2_{i+1/2}}{v_i \Delta r}\,\frac{2}{\exp(-\Delta W_{i+1})+1}, \quad (32)$$

$$c_i = \frac{r^2_{i-1/2}}{v_i \Delta r}\,\frac{2}{\exp(-\Delta W_i)+1} + \frac{r^2_{i+1/2}}{v_i \Delta r}\,\frac{2}{\exp(+\Delta W_{i+1})+1}. \quad (33)$$

It can be easily seen that the proposed scheme, all coefficients have a definite sign (positive), with the magnitudes bounded above and related to each other by simple relations. Now for this stable scheme we can easily use relatively large value of the time increments.

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