Computer modeling and simulation of electrically charged nano/micro-particles interaction into aqueous solution by the Brownian dissipative dynamics of their atomic counterions ensemble

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Abstract. On the basis of free energy functional of charged ions and equation of diffusion of ions in self-consistent electric potential, a method of Brownian dissipative dynamics of ions near electrically charged colloidal micro/nano-particles in aqueous solution or dusty plasma particles in the air is proposed for investigation of ionic atmosphere structure near charged surfaces, and electric interparticle force is calculated.

1. Introduction

Formation of ionic crystals (such as NaCl), colloidal crystals self-assembly, and dusty plasma particles’ (macroions) ordered structures indicates the existence of an energy minimum for ion-counterion system, and hence the attraction of similarly charged particles mediated by their counterions. Some experiments show that interacting electrically charged colloidal particles with diameters of 10-1000 nm in aqueous solution with small compensative counter-ions demonstrate the long range attraction and form the colloidal crystals if the concentration of additional electrolyte (salt) is low enough. The dusty plasma particles (macroions) demonstrate the analogous behavior and form the ordered structures in ionized air.

The first part of researchers argues that the attraction describes by only dispersion forces. Another part has suggested the non-DLVO (Derjaguin-Landau-Verwey-Overbeek) approaches with electrical long range attraction obtained from Poisson-Boltzmann equation (PBE) solution [1] or from novel free energy of ions consideration [2-5].

A simple model of salt-free electrolyte with a strong asymmetry of charge and size of the constituent particles, macroions and counterions, is in the area of fundamental interests of many modern theoretical and experimental researches. For example, work [6] reports a novel phenomenon of a surface-induced phase transition in salt-free solutions of charged colloids. Experimental investigation the properties and applications of aqueous charge-stabilized colloidal solution without side electrolyte was reported in [7].

PBE solution shows that the attraction is possible if the counterions are concentrated mostly between the interacting colloidal particles, and electric interparticle force can be calculated.
analytically. Two flat parallel plates, having the same sign of surface charge density, electrically attract each other if the space lying between plates is filled with the neutralizing counterions. The attractive force acting to the unit of surface area is $f = -\sigma^2(2\varepsilon\varepsilon_0)^{-1}$, where $\sigma$ is surface charge density distributed on the plate; $\varepsilon$ and $\varepsilon_0$ are the dielectric constants of continuous media around the plates and of vacuum respectively. On the contrary, an electric repulsion takes place always if these counterions have filled both the space between the plates and all space outside the plates. In analogous case, analytical solution of PBE does not exist for charged cylinders or spheres.

Currently there are many interesting works dedicated to derivation the ordinary PBE and its modifications from statistical field theory. The PBE is a mean-field approximation of statistical ensemble of point-like ions. The modifying PBE in the context of dense ionic liquids where steric effects become important was studied in [8]. Authors of that work elucidate how equivalent convex free energy functions can be constructed to describe steric effects in a manner, which is more convenient for numerical minimisation. In work [5], a non-linear integro-differential equation was obtained with respect to the mean-field electrostatic potential, generalizing the Poisson-Boltzmann-Langevin equation for the point-like dipoles obtained first in [9].

We guess, it is clear that self-consistent insertion the PBE into framework of the classic electromagnetic theory of field could be useful due to opportunity to develop well-justified further modifications of the PBE with taking into account the features, which did not included in ordinary PBE. In this work, it is shown that ordinary PBE can be obtained in form of Lagrange equation by standard Lagrange’s procedure of the field theory ([10], p.77). The Lagrangian of equilibrium system of charged particles and counterions with Maxwell-Boltzmann energy distribution of counterions is considered. This Lagrangian was derived from the chemical potential of the counterion including the electrostatic term (Coulomb interaction of the given counterion charge with all other charges of the system) and entropy term which corresponds to an ideal gas (or ideal solute). In such a model, steric effects between neighboring counterions, which are treated as point-like particles, do not take into account. The medium is modeled by a homogeneous and isotropic dielectric constant.

Here is shown, that ordinary PBE corresponds to mean-field of the equilibrium state of Brownian ensemble of small counterions in the self-consistent electric field of these counterion and macroions (micro/nano-particles).

In our model, the steric effects can be taken into account by introducing of the finite radius of counterion. On the basis of free energy functional of charged ions and equation of diffusion of ions in self-consistent electric potential, a method of Brownian dissipative dynamics of ions near electrically charged colloidal micro/nano-particles in aqueous solution or dusty plasma particles in the air is proposed for investigation of ionic atmosphere structure near charged surfaces, and electric interparticle force is calculated.

2. Model
Let us consider dilute aqueous solution of colloidal particles ($R$ denotes the radius of particle) with fixed uniformly distributed surface electric charge $Q = Ze$, where $e$ is elementary charge, $Z \gg 1$. The total charge of solution is zero due to the presence of small counterions with the charge of $q = -ze$, where $z$ is small natural number; then $Q = -Nq$, where $N = Zz^{-1}$. Let $a$ denotes the radius of counterion; $a << R$, so that one can suppose that the Brownian motion of the colloidal particles is negligibly small, but each counterion moves in self-consistent electric field of particles and other counterions under action of Brownian force. In frameworks of such adiabatic approximation, one can assume that counterions are founding the quasi-stationary atmosphere around motionless colloidal particle (figure 1).
The big ion (colloidal particle) and its counterions atmosphere.

Figure 1.

The methods determining the average concentration of counterions near particle can be divided into two categories: kinetic, based on equation of counterions diffusion in self-consistent electric potential of all counterions and the big motionless colloidal particle; dynamical, based on Lagrange equations of motion obtained from the Lagrange’s variation principle. Counterionic current density can be written as

$$ j = -D \nabla n - nb \nabla U, \quad (1) $$

where $D$ is diffusion coefficient, $n$ is counterions concentration, $U$ is potential energy of self-consistent electric field, $b = \frac{D}{kT}$ is counterion mobility describing by Einstein equation ($k$ is Boltzmann constant, $T$ is temperature). Equation of continuity of current (1) is

$$ \frac{\partial n}{\partial t} = \nabla \left[ n D \left( \nabla \ln n + (kT)^{-1} \nabla U \right) \right]. \quad (2) $$

Chemical potential of counterion is given by

$$ \mu = kT \ln \left( \frac{n}{n_0} \right) + q \varphi_0 + \frac{1}{2} q \varphi_i, \quad (3) $$

where $\varphi_0$ is Coulomb potential of spherical particle (figure 1), $\varphi_i$ is self-consistent electric potential of counterions atmosphere. Poisson equation gives

$$ \nabla^2 \varphi_i = -\frac{q n}{\varepsilon \varepsilon_0}, \quad (4) $$

where $\varepsilon$ is dielectric permittivity of solution.

To determine the potential energy $U$ which corresponds to Eq. (3), we have to obtain the Lagrange’s equations for next Lagrangian

$$ L = n \mu = n \left( kT \ln \left( \frac{n}{n_0} \right) + q \varphi_0 + \frac{1}{2} q \varphi_i \right) \quad (5) $$

The variational procedure, describing by equation

$$ \delta \int \left[ \int \left( nkT \ln \left( \frac{n}{n_0} \right) + \rho \varphi_0 + \frac{1}{2} \rho \varphi_i \right) dV \right] = 0, \quad (6) $$
minimizes the chemical potential of counterions system in the external electric field of colloidal particle. With account of electric field strength determination according by equations
\[ E_i = -\nabla \phi_i, \quad E_0 = -\nabla \phi_0, \]
(7)
after integration by parts, integral in Eq. (6) can be rewritten as
\[ \delta \int \left( \varepsilon \varepsilon_0 kT \frac{\varepsilon E_0}{q} \nabla E_i \ln \left( \frac{\varepsilon \varepsilon_0}{q n_0} \nabla E_i \right) + \varepsilon E_0 \varepsilon E_i E_0 + \frac{1}{2} \varepsilon E_0 E_i^2 \right) dV = 0, \]
(8)
where we substituted concentration of counterions from Poisson equation,
\[ \n = \frac{\varepsilon \varepsilon_0}{q} \nabla E_i, \]
(9)
Lagrange equations for variational principle given by Eq. (8) has a form
\[ \frac{\partial \hat{L}}{\partial E_{ia}} = \frac{\partial}{\partial x_\beta} \left[ \frac{\partial \hat{L}}{\partial E_{ia}} \left( \frac{\partial}{\partial x_\beta} \right) \right], \]
(10)
where modified Lagrangian, \( \hat{L} \), is integrand of Eq. (8); \( \alpha \) and \( \beta \) can independently take the natural values 1,2,3, which denote the Cartesian space projections of vector. One can easily show that solution of Eq. (10) determines by expression
\[ n = n_0 \exp \left( -\frac{q(\phi_0 + \phi_i)}{kT} \right). \]
(11)
On the other hand, the equilibrium state requires the condition \( j = 0 \) in Eq. (1), which gives the analogous expression
\[ n = n_0 \exp \left( -\frac{U}{kT} \right), \]
(12)
whence
\[ U = q \phi_0 + q \phi_i. \]
(13)
Substituting (10) in Poisson equation (3), one can obtain the Poisson-Boltzmann equation
\[ \nabla^2 \phi_i = -\frac{\rho_0}{\varepsilon \varepsilon_0} \exp \left( -\frac{q(\phi_0 + \phi_i)}{kT} \right). \]
(14)
Thus, it was shown that PBE can be considered as equilibrium form of equation of charged particles diffusion in their self-consistent electric field. The general case of non-equilibrium ensemble of counterions evolution is describing by Eq. (2). The Langevin equation which corresponds to diffusion equation (2) can be written as
\[ m \frac{dv}{dt} = -\frac{m kT}{D} v - q \nabla (\phi_0 + \phi_i) + F_{nc} + F_B, \]
(15)
where \( m \) is an effective mass of given counterion; \( F_{nc} \) is the sum of all non-electrostatic forces including the rigid wall interacting potential between particle and counterion; \( F_B \) is the
Brownian force which describes by Markov’s random process with zero mean, and it satisfies the equation

$$< F_{\alpha\beta}(t), F_{\beta\alpha}'(t') > = 2kT\delta(t-t')\delta_{\alpha\beta},$$

(16)

where $\alpha$ and $\beta$ designate the Cartesian projections symbols, and the brackets denote the average over an equilibrium ensemble.

3. Calculation results
Geometry of model system is presented in figure 2 a. In the numerical experiments we used the next values of parameters: $H = 1000$ nm, $R = 500$ nm, $0.5 \ R + L = 1000$ nm, counterion radius is $0.5$ nm; counterion charge is $-2$ e, total number of counterions is 4000, dielectric permittivity of solvent is 81 (aqueous solution) with temperature of 295 K. Visualization (by the program VMD 1.8) of counterions ensemble near interacting particles obtained in numerical experiment is given in figure 2 b).

![Figure 2](image)

**Figure 2.** a) Geometry of space region occupied by both interacting particles and their counterions. b) Visualization of counterions ensemble near interacting particles.

![Figure 3](image)

**Figure 3.** Electrostatic force acting to the particle if interparticle distance is 2400 μm (a) and 1400 μm (b).

The value of interaction force between two particles with account of counterions ‘atmosphere’ is shown in figure 3 for two distances between the centers of the particles. The negative sign of the force means the effective attraction between the particles due to counterions screening of their initial Coulomb repulsion. Our result confirms the conclusions of the work [1]. The attraction of equally charged spheres in a cloud of their counterions is possible.

In this paper, we have tested a method for calculating the interaction of colloids using the Brownian dynamics of counterions. Obviously, it was shown that this approach can be applied to the solution of the problem. However, obtained result has a preliminary character, and it has to be
rechecked and corrected during more detail calculations including total free energy surface drawing, entropy and adsorption terms estimations. We are supposing to do that in our next works.

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