Charged colloidal system: Small ion distribution and effective interaction

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HIGHLIGHTS

- Screening by counterion becomes more complete for larger macroion charge.
- Chemical potential of small ions is constant throughout the system.
- Effective interaction between two macroions of same charge is normally repulsive.
- Effective interaction is similar to the usual models with renormalized charge.
- Many-body effect is attractive for short distance.

GRAPHICAL ABSTRACT
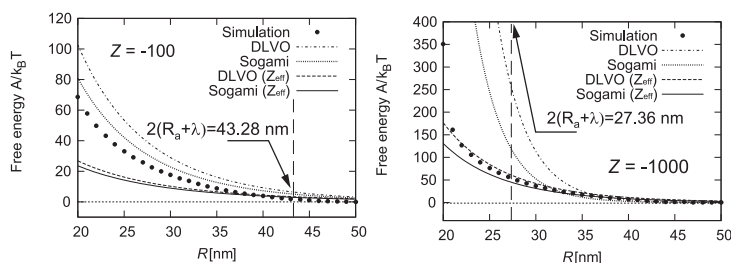
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ABSTRACT

We applied a molecular dynamics simulation technique to charged colloidal systems in order to investigate small ion distribution in thermal equilibrium and to evaluate the effective interaction among macroions. For a system containing a single macroion, screening by counterions was evaluated. The screening becomes more complete for larger macroion charge. In spite of the large inhomogeneity, the chemical potential of small ions is constant for the entire system. Using a thermodynamic integral method, the effective potential (Helmholtz free energy) for two-macroion systems was evaluated as a function of macroion separation distance, and found to be repulsive under normal conditions. Many-body effect is also discussed by comparing the effective potentials for two- and three-macroion systems.

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1. Introduction

Charged colloidal systems (latexes, metal nanoparticles, proteins, etc.) have been widely studied in various fields of science and engineering. Among many interesting phenomena, they have an ordered or crystalline state under some conditions to show iridescence. It is conventionally explained with the DLVO theory [1,2], which takes account of repulsion due to the overlap of electric double layers and the van der Waals attraction. When the salt concentration is very low, the screening by counterions is incomplete, causing strong repulsive interaction. The crystallization is then the Alder type transition [3,4]. Upon adding more salt, however, the crystalline structure disappears [5], contrary to the theoretical prediction of entrapment in a potential minimum. Sogami and Ise have proposed a model [6,7] that explains the phenomena with electrostatic interaction only. They gave an analytic expression for the Gibbs free energy of the system and showed that electrostatic attraction can exist between macroions of same charge. It has been long controversial, but some recent experiments seem to support the concept of electrostatic attraction [8]. Another theoretical aspect is the treatment of the Poisson–Boltzmann equation. Conventionally a linearization approximation has been adopted with implicit assumption of weak interactions. Akiyama et al. [9] recently reported based on an integral equation approach (an

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Nomenclature

A free energy or effective potential (J)
e elementary charge (C)
F force (N)
k_B Boltzmann constant (J/K)
l distance between macroion surface and a small ion (m)
m mass of a small ion (kg)
n number density (m^{-3})
N number of particles
p momentum of small ion ((kg m)/s)
P pressure (Pa)
q charge of a small ion (C)
Q_N partition function
r distance from the center of a macroion (m)
R distance between macroions (m)
R_a macroion radius (m)
T temperature (K)
U potential energy (J)
V volume (m^3)
Z a macroion charge (valence)

Greek letters
ϵ Lennard–Jones energy parameter (J)
ϵ_w permittivity of water (F/m)
ϕ interaction potential between particles (J)
λ Debye screening length (m)
Λ thermal de Broglie wavelength (m)
μ chemical potential (J)
σ Lennard–Jones size parameter (m)

superscript
c   Coulombic
ext   external pressure
LJ   Lennard–Jones

subscript
eff   effective charge
ex   excess term
i ith species of small ions
id   ideal gas term
m   macroion
run   running sum
s   small ion
vi   virial term
0   average over the simulation cell

Ornstein–Zernike equation combined with hypernetted-chain closure) without the linearization that an attractive interaction between macromolecules appears in some range of salt concentration.

In this paper, we adopt a molecular simulation approach to investigate charged colloidal systems. Our main objective is to estimate the effective interaction between two macroions of same charge. For that purpose, we carry out a series of molecular dynamics simulations for small ions with macroions of fixed positions. With a similar approach, we also investigate small ion distribution around a single macroion to see the screening. Since the difference between the DLVO theory and other models would be relevant under the low salt concentration conditions, we have done most of the simulations with salt-free systems.

2. Simulation method

We adopted a simple canonical ensemble molecular dynamics (MD) simulation for small ions, assuming that solvent (water) is just a medium with appropriate permittivity. A Brownian dynamics (BD) technique [10] is another candidate, but both methods should give the same static properties (ion distributions and effective force on macroions) at equilibrium states.

We assume that the potential energy of the system is a sum of two-body functions:

$$U = \sum_{i,j}[\phi_{ss}^c(r_{ij}) + \phi_{ss}^{LJ}(r_{ij})] + \sum_{i,k}[\phi_{sm}^c(r_{ik}) + \phi_{sm}^{LJ}(r_{ik})] + \sum_{k,l}\phi_{mm}^c(r_{kl}) \tag{1}$$

where i and j represent small ions, k and l represent macroions. The subscripts s and m correspond to small ions and macroions, respectively. The Coulombic interaction between ith (small or macro) ion with charge q_i and jth with q_j is

$$\phi^c(r_{ij}) = \frac{1}{4\pi\epsilon_w}\frac{q_i q_j}{r_{ij}} \tag{2}$$

where $\epsilon_w = 80.4\,\epsilon_0$ is the permittivity of water at room temperature (ϵ_0: vacuum permittivity).

The short-range Lennard–Jones (LJ) type interaction is assumed only for s–s and s–m. We assume no LJ interaction between macroions because its interaction range is much shorter than the Coulombic one. If necessary, we can take account of a dispersion force after the simulation when the effective interaction is evaluated.

Often used in theoretical studies [11,9] and Monte Carlo simulations [11–14] is the primitive model (PM), where hard core repulsive interactions are considered as well as the Coulombic ones between small ions and macroions. In the MD simulations, discontinuous interactions are less preferable. The LJ interaction is more convenient also in evaluation of a depletion force, which arises from the asymmetric distribution of small ions around macroions.

For the interaction between small ions, we use a conventional LJ (12-6) potential depending on the particle distance r as:

$$\phi_{ss}^{LJ}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] \tag{3}$$

where ϵ_{ij} and σ_{ij} are the LJ parameters. Since macroions are sufficiently larger than small ions, the LJ interaction between a small ion and a macroion is given by integrating the LJ (12-6) potential in a semi-infinite space, leading to:

$$\phi_{sm}^{LJ}(l) = 8\pi\epsilon_m n_m \sigma_m^3 \left[\frac{1}{90}\left(\frac{\sigma_m}{l}\right)^9 - \frac{1}{12}\left(\frac{\sigma_m}{l}\right)^3\right] \tag{4}$$

as a function of the distance l from the macroion surface, where ϵ_m and σ_m are the LJ parameters for macroions, and n_m is the number density inside the macroion.

In this study, we assume that the macroions (colloid particles) are polyacrylic acid (PAA) anions with constant charge $-Ze$ (e: elementary charge) being uniformly distributed in each sphere of radius R_a. Counterions are then cations and sodium ions (Na$^+$) are assumed, while chloride ions (Cl$^-$) are used for coions. Parameters are listed in Table 1. The Lorentz–Berthelot combination rule is assumed for LJ parameters between different species:

$$\begin{cases} \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \\[2mm] \sigma_{ij} = \dfrac{\sigma_i + \sigma_j}{2} \end{cases} \tag{5}$$