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Ion size effect on colloidal forces within the primitive model

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The effect of ion size on the mean force between a pair of isolated charged particles in an electrolyte solution is investigated using Monte Carlo simulations within the framework of the primitive model where both colloidal particles and small ions are represented by charged hard spheres and the solvent is treated as a dielectric continuum. It is found that the short-ranged attraction between like-charged macroions diminishes as the diameter of the intermediating divalent counterions and coions increases and the maximum attractive force is approximately a linear function of the counterion diameter. This size effect contradicts the prediction of the Asakura-Oosawa theory suggesting that an increase in the excluded volume of small ions would lead to a stronger depletion between colloidal particles. Interestingly, the simulation results indicate that both the hard-sphere collision and the electrostatic contributions to the mean force are insensitive to the size disparity of colloidal particles with the same average diameter.

Key words: *colloids, electrostatic interactions, Monte Carlo*

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1. Introduction

Talking about how a pair of particles interact with each other in a solvent, probably no other person knows it better than Doug Henderson, a contemporary legend in the field of liquid-state theory. A thorough review of his contributions to this area is not attempted here because that would easily take several volumes! Thanks to his mounds of classical publications, [1–23] we now have much improved understanding of colloidal forces, in particular, regarding the effects of solvation, electrostatics, excluded volume, and interactions between colloidal particles in a polymerizing solvent.

Theoretical description of the electrostatic interactions between a pair of charged particles in an electrolyte solution often starts with the Poisson-Boltzmann equation, a mean-field theory that neglects the size effect and the correlation of small ion distri-

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butions [7]. The Poisson-Boltzmann equation, as well as its approximated analytical solution given by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (1940s), provides a semi-quantitative description of the solvent-mediated potential between charged colloidal particles. However, as early as 1930s, the mean-field description was questioned by prominent researchers including Langmuir and Kirkwood [24]. Langmuir argued that because of the intervention of small ions of opposite charge or counterions, there could exist an electrostatic attraction between like-charged particles at certain solution conditions. The electrostatic attraction between like charges directly contradicts the prediction of the Poisson-Boltzmann equation, which states that the average solvent-mediated electrostatic potential between two macroions of similar charge is always repulsive. Kirkwood and Schumaker developed an analytical expression for the attractive force and demonstrated that the fluctuations in the net charges of macroions result in an attractive potential. In the late 1960s, Oosawa demonstrated that the correlated fluctuations of the small ion distributions around two macroions could lead to an electrostatic attraction [25]. Moreover, Sogami and Ise proposed a variation of the DLVO theory based on the Gibbs free energy. As far as it predicts a ubiquitous long-range attraction between like charges [26], the Sogami-Ise theory has ensured lots of controversies ever since it was published.

Molecular simulations were applied to the study of interaction between infinitely-large, parallel charged plates first by Guldbrand et al. [27], and a few years later by Valleau et al. [28]. Both groups indicated that in contrast to the prediction of the DLVO theory, the electrostatic force between like-charged plates turns out to be almost everywhere attractive in the presence of multivalent counterions. Electrostatic attraction between like-charged macroions of other geometries such as cylinders and spheres has also been demonstrated in recent years using either Monte Carlo or molecular dynamic simulations [29–39]. These simulation results have settled down substantial controversies in the colloid literature on attraction between like charges and more importantly, provide benchmark data for the development of an improved theory for colloidal interactions.

Amid numerous theoretical efforts toward an improved theory for colloidal forces, the integral equation approaches pioneered by Henderson and coworkers might be most promising [1,5,6,9,11,14,16,17,20–22,40–44]. Some other methods have also been proposed in the literature. For instance, both anisotropic hypernetted-chain theory [45] and density functional theory [46,47] have been applied to the calculation of the interaction force between charged plates. After much computational effort, both theories were found in good agreement with simulation results. However, due to the numerical difficulties, extension of similar approaches to macroions of other geometry has not been reported. For interaction between cylindrical colloidal particles, Ha and Liu proposed a field-theory approach taking into account the electrostatic attraction. These authors indicated that, as elucidated by earlier investigations [25,27], the attraction between like charges resembles the van der Waals attractions between spherical molecules of nonpolar species such as argon [48]. However, the field-theory calculation was followed by criticisms of Levin and others [49,50]. For interaction between spherical macroions, Netz and Orland proposed a correction term to the

DVLO theory based on a third-order cumulant expansion [51]. This additional term introduces attractive contributions but vanishes for interaction between two isolated colloidal particles in an electrolyte solution.

Unlike the DLVO theory, most modern approaches for representing the colloidal forces explicitly take into account both the size and valence of small ions. Consequently, the overall potential between colloidal particles includes at least two parts, one due to the particle size and the other due to the electrostatic interactions. Whereas most previous investigations have been focused on the electrostatic effects, much less attention is given to the role of ion diameter on the overall force between colloidal particles and the interplay between the excluded volume and electrostatic interactions of intermediating small ions. For an electrostatically neutral system, a fair understanding of the excluded-volume effect is provided by the phenomenological theory of Asakura and Oosawa (AO) based on a simple geometry argument [52]. The AO theory predicts that the excluded-volume effect introduces an effective attraction between colloidal particles within the range of the size of the intermediating species. For colloidal particles surrounded by neutral species, the prediction of the AO theory is in semi-quantitative agreement with more recent molecular simulations [53]. While the entropically driven excluded effect is well understood at least for uncharged systems, it is much less apparent if the intermediating species are also charged or coupled with other force fields. In principle, both integral equation theories and density functional theories are capable of treating the excluded-volume effects and electrostatics separately. Regrettably, most previous investigations assumed that the diameter of small ions is fixed (round 4.25 Å), appropriately equal to the diameter of a solvated ion in water. Quite recently, the ion size effect on the diffuse potential and ion distributions of planar electric double layers was investigated using Monte Carlo simulation and the HNC/MSA integral equation theory [54]. A major conclusion from this work is that for realistic hydrated ions of 2:1 electrolytes, the decrease of the diffuse potential with an increasing surface charge density as predicted by the integration theories was not observed in Monte Carlo simulations. A systematic investigation on the effect of ion size on colloidal forces was not explored.

In this work, we report the results from Monte Carlo simulations examining the effect of the excluded volume of intermediating small ions on colloidal forces within the primitive model. Special attention is given to the interplay between the electrostatic and excluded-volume contributions to the overall forces.

2. Simulation techniques

We consider the mean force between a pair of uniformly charged colloidal particles dispersed in a symmetric electrolyte solution containing divalent counterions and coions. In the primitive model, the colloidal particles as well as the counterions and coions are represented by hard spheres of different diameters and valences, and the solvent is represented by a dielectric continuum. The NVT-ensemble Monte Carlo simulation is used to calculate the collision and electrostatic forces between the isolated colloidal particles intermediated by small ions [33]. Specifically, for each separation of colloidal particles, NVT simulation is applied to a cubic simulation box containing 80 counterions, 60 coions, and two identical negatively charged macroions. The macroions are placed along the box diagonal in order to minimize the boundary effect. The three-dimensional periodic boundary conditions are applied to all simulations and the long-ranged Coulomb interactions are calculated using the Ewald sum method. Due to the charge of macroions, there is a small difference in the concentrations of counterions and coions in order to keep the condition of electrostatic neutrality.

Table 1. The diameters of small ions (σ_s) and macroions (σ_1 and σ_2) and the valence of macroions for the various runs performed to calculate the force between two macroions with charge fixed at the center.

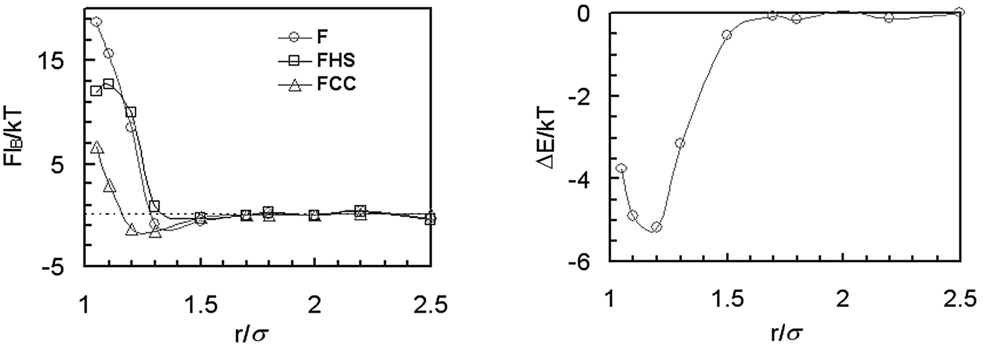
Runs	σ_1(Å)	σ_2(Å)	Z_1	Z_2	σ_s (Å)
A	20	20	–20	–20	2
B	20	20	–20	–20	4
C	20	20	–20	–20	5
D	20	20	–20	–20	6
E	18	22	–18	–22	5
F	20	20	–20	–20	5
G	16	24	–16	–24	5

Throughout this work, the concentration of electrolyte is fixed at $C = 0.06$ M and the permittivity "ε" of the solvent and solutes corresponds to that of water at ambient conditions. The box length is fixed at 118.4 Å, approximately 20 times of the Debye length of small ions (≈ 6.2 Å). As a result, the correlation between macroions in image simulation boxes is negligible, i.e., the system mimics the interaction between colloidal particles at an infinite dilution. Table 1 summarizes the simulation parameters for the different conditions investigated in this work. Further details on the implementation of the Monte Carlo simulation are provided in our previous publications [30,33–35,37].

In calculating the average colloidal forces for each separation of colloidal particles, we assume that the system attains equilibrium after approximately $5 \cdot 10^5$ moves per particle and up to a million moves per particle are used for sampling the hard-sphere collision and electrostatic forces. All calculations were performed using IBM SP RS/6000 computers from the National Energy Research Scientific Computing Center (NERSC).

3. Results and discussion

Figure 1a presents the overall (F), hard-sphere (F_{hs}), and electrostatic (F_{cc}) mean forces between a pair of macroions of valance $Z_{\mathrm{M}} = -20$ and diameter $\sigma = 20$ Å in an aqueous solution of 2:2 electrolyte solution. Here l_{B} stands for the Bjerrum



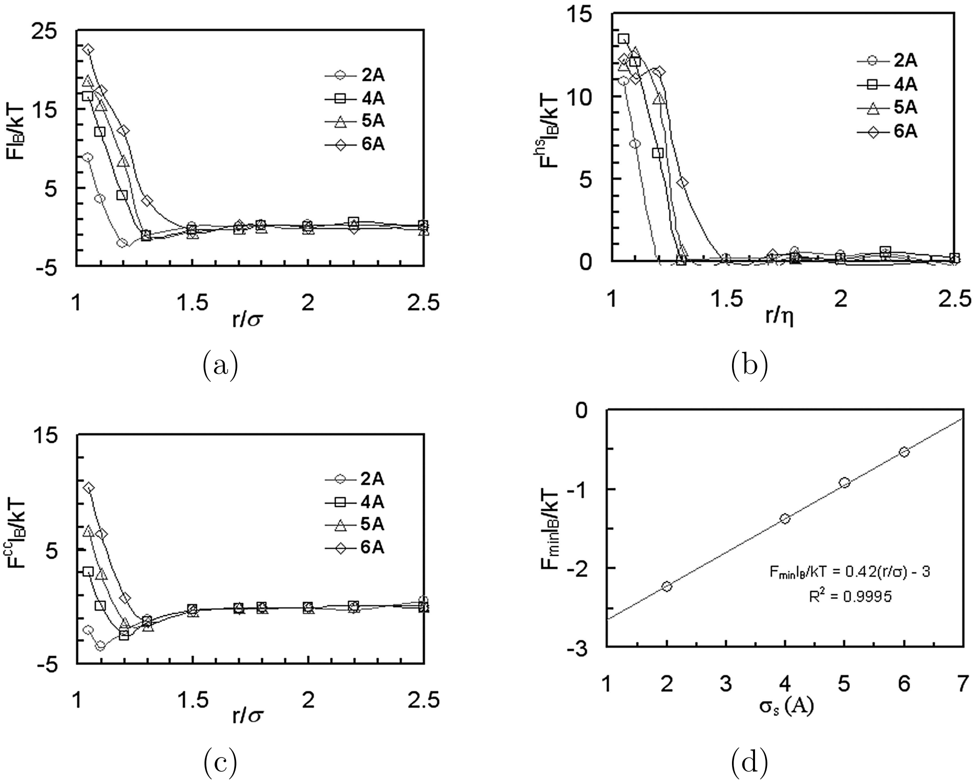
(a)   (b)

Figure 1. (a) The total force (○) as well as the hard-sphere contribution (□) and the electrostatic contribution (△) for the interaction between two identical macroions in a 2:2 electrolyte solution (Run C). (b) The relative internal energy as a function of the center-to-center separation between macroions. All lines are for the guidance of the eye.

length, defined as the average separation between two unit charges where the electrostatic potential is equal to the thermal energy kT. For an aqueous solution at ambient condition, $l_B = 7.8$ Å. The divalent counterions and coions have the same diameter of 5 Å. As observed in our previous simulations, [30,33–35,37] the overall force between like-charged macroions is repulsive near the contact, turns into attraction when the surface-to-surface distance is of the diameter of the counterions, and monotonically decays at larger separations. The maximum attraction occurs approximately at a surface-to-surface separation that is sufficient to accommodate a monolayer of counterions.

The appearance of the short-ranged attraction is due to the correlated fluctuations of small ion distributions that are ignored completely in the DLVO theory. While the origin of this attraction is now well understood, at least qualitatively, and the force profile or potential of mean force can be semi-quantitatively captured using the aforementioned integral equation theories or density functional theories, quantitative descriptions of the hard-sphere collision and electrostatic mean forces for spherical macroions in an electrolyte solution remains theoretically challenging even within the primitive model. Different from the predictions of the AO theory, the hard-sphere collision is purely repulsive at essentially all ranges of inter-particle separations. For interactions between colloidal particles surrounded by neutral species, the intermediating species distribute almost uniformly around the colloidal particles and an entropic depletion attraction is induced due to the overlap of the depletion layers of the individual particles. For macroions dispersed in an electrolyte solution, however, the counterions as well as coions are crowded in the space between the macroions, leading to an osmotic repulsion. Intuitively, the short-ranged hard-sphere repulsive force can be understood by the fact that a higher concentration of small ions in the space between macroions causes more collisions of small ions, and thereby driving the macroions apart.

The electrostatic contribution of the mean force is also repulsive near the contact and turns into attraction at small separations of macroions. The strong repulsion near the contact of macroions is mainly due to the bare charge effect and the short-ranged attraction is due to the fluctuation of charge distributions. The effect of electrostatic energy on the mean forces is most clearly seen in the plot of relative internal energy as a function of distance, $\Delta E(r)$, as depicted in figure 1b. Here $\Delta E(r)$ is defined as the internal energy of the system when the two macroions are kept at a center-to-center distance r minus that of the system when the macroions are infinitely apart. Apparently, only the electrostatic interactions directly contribute to $\Delta E(r)$. Interestingly, $\Delta E(r)$ is always negative at all separation of macroions, indicating that small separation of macroions is energetically favorable but entropically unfavorable. It other words, the repulsive potential between similar charged macroions is mainly due to the entropy penalty for the localization of small ions.



(a) (b)

(c) (d)

Figure 2. The total (a), hard-sphere (b), and electrostatic (c) force profiles between two identical macroions in a 2:2 electrolyte solution with microions of different sizes. (Runs A-D) (d) The correlation between the maximum attractive (or minimum) force between macroions and the diameter of surrounding small ions.

A comparison of the force and energy profiles indicates that there is a direct correlation between the ranges of attractive and repulsive mean electrostatic forces and the slope of $\Delta E(r)$. It suggests that the mean-electrostatic force between macroions is mainly determined by the energy effect. The attraction between like charges is most probable when the macroions are dispersed in electrolyte solutions containing multi-valent counterions. For instance, at ambient conditions of aqueous solutions, the mean force between like charged particles is always repulsive if the counterions are monovalent and the strength of attraction increases with the counterion valence.

Figure 2a depicts the mean forces between macroions for 4 different diameters of the intermediating counterions and coions while all other solution conditions remain the same. As the diameter of small ions increases, the mean force becomes more repulsive near the contact and the shallow attractive well shifts outward and eventually diminishes. Due to the strong coupling of the electrostatic and excluded-volume interactions, the size effect is entirely different from the prediction of the AO theory. Intuitively, one expects that the stronger repulsion at short separations should be attributed to the higher probability of collision as the size of small ions grows. However, a close inspection of figures 2b and 2c for the collision and electrostatic contributions of the mean forces indicates that the size mainly affects the range rather than the strength of the repulsion. The electrostatic forces exhibit a behavior similar to that for the overall forces. Most surprisingly, it appears that there is a linear correlation between the maximum attraction and the size of small ions, as shown in figure 2d. We suspect that the linear relation is due to the relatively small change of the ion diameter investigated in this work.

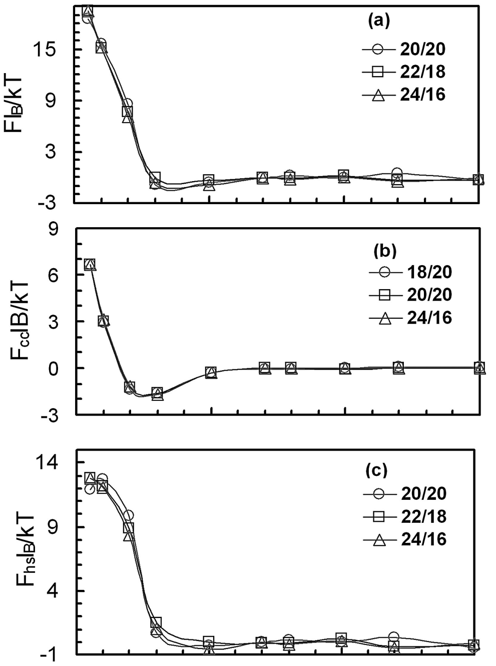


Figure 3. The force profiles between macroions of different diameters in a 2:2 electrolyte solution.(Runs E-G) Here σ stands for the average diameter.

Intuitively, one may expect that at similar solution conditions, the average force would be sensitive to the size and charge density of interacting macroions. To test this speculation, we calculate the mean forces between three pairs of macroions of different sizes but the same average diameter (Runs E-G). Figure 3 presents the force profiles as well as the excluded volume and electrostatic contributions. Here the diameter of divalent small ions is fixed at 5 Å. Apparently, the overall force profile as well as the individual excluded volume and electrostatic contributions are essentially independent of the disparity in macroion size and charge as long as the average values are fixed. Even though the behavior is consistent with the prediction of the DLVO theory, this observation is somewhat counterintuitive because even at the same average diameter and charge the total surface area of macroions varies with the disparity of the macroion pairs, leading to the change in both the probability of collision and the charge density at the macroion surface. Therefore, we suspect that the results might be quite different when the macroions are highly asymmetric in both valence and size.

4. Conclusions

Monte Carlo simulations are applied to the investigation of the effect of ion size on the mean force between a pair of macroions in various electrolyte solutions. We find that both the electrostatic and hard-sphere collisions are sensitive to the ion size. In divalent electrolyte solutions, the short-ranged attraction between macroions diminishes as the diameter of intermediating small ions increases. This size effect is totally different from the prediction of the AO theory, which is applicable only to interactions between colloidal particles surrounded by neutral species. Within a small variation of the size of intermediating small ions, the maximum attractive force between like charges linearly correlates with the ion diameter. This suggests that the negligence of the ion size will enhance the attraction due to the fluctuation of small ion distributions. The simulation results also suggest that at similar solution conditions, the mean force between like-charged macroions appears relatively insensitive to the size and charge disparity of macroions as long as the average values are fixed.

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Вплив іонних розмірів на взаємодії між колоїдами в рамках примітивної моделі

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Вплив розмірів іонів на потенціал середньої сили між парою ізольованих заряджених частинок досліджується за допомогою Монте Карло симуляцій в рамках примітивної моделі, в якій як колоїдні частинки, так і малі іони є представлені зарядженими твердими сферами, а розчинник трактується як неперервне діелектричне середовище. Показано, що короткодіюче притягання між однаково зарядженими макроіонами зменшується, якщо діаметр двовалентних контраіонів та коіонів збільшується, а максимальна сила притягання є приблизно лінійною функцією діаметру контраіонів. Такий вплив розмірів протирічить передбаченням теорії Асакури-Оосави, які вказують на те, що збільшення виключеного об'єму малих іонів веде до сильнішого притягання між колоїдними частинками. Відмічено, що комп'ютерні результати показують, що як твердосферні зіткнення, так і вклади електростатичних взаємодій до потенціалу середньої сили є нечутливими до відмінностей у розмірах колоїдних частинок, якщо середній розмір є однаковим.

Ключові слова: *колоїди, електростатичні взаємодії, Монте Карло*

PACS: *61.20.Ja, 82.70.Dd*