Molecular simulation of charged polymers: the interplay between electrostatic and entropic effect

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Dendrimers are highly-branched treelike macromolecules. They are nano-sized, and have a spherical shape, which are representative of *soft-colloidal particles*. Dendrimers have numerous potential applications such as contrast agents for visualizing blood streams in magnetic resonance imaging (MRI), and drug-delivery systems. We can expect different physical properties and structural formations from those in hard-sphere suspensions. The effective interaction between dendrimers gives useful information to understand the phase behaviors in solution, which have been recently investigated by small-angle x-ray scattering (SAXS) experiments. The effect of many-body interaction among dendrimer molecules on the phase behavior is an interesting problem, especially in a dense solution.

Several numerical studies have been devoted to the properties of many-body interactions to determine the structural formation in colloidal suspensions. These studies show that the pair interaction between charged colloidal particles is found to be repulsive, consistent with traditional DLVO theory. In this case, the triplet potential becomes attractive due to the presence of a charged colloidal particle between the other two particles that shields the direct repulsive interaction between the latter two. In addition, the effect of attractive interaction on the phase behavior of charged colloidal suspensions have been studied numerically. On the basis of free energy calculations, it is shown that the bcc phase is stabilized by long-range repulsions, and the inclusion of triplet attraction reduces the stability of the bcc phase. These studies imply that the triplet interaction gives a significant effect on the phase diagram of charged colloidal suspensions. It is of great interest to clarify the phase diagram of "soft colloidal crystal".

At first, we investigate a pair of dendrimer molecules which are confined in a cubic box by molecular dynamics simulation. The long-range nature of the Coulomb interaction is numerically treated by Lekner summation method with particle-cell acceleration technique[1]. A pair of dendrimers (N=2) is placed symmetrically along the body diagonal of the cube, such that the center of the cube coincides with the center of mass of the two molecules. Furthermore, the box contains N_c counterions carrying an opposite charge when the two dendrimer molecules are charged. Secondly, we also consider the three-body case of (N=3) in a cubic box. The positions of the centers of the dendrimers are given such that they form an equilateral triangle of length r. In Fig. 1, open squares and open circles show the calculated result of effective forces $F^{(2)}(r)$ with N=2, and $F^{(3)}(r)$ with N=3, respectively. The inset of Fig. 1 shows the triplet force $\Delta F(r)$ defined to be $\Delta F(r) \equiv F^{(3)}(r) - \sqrt{3}F^{(2)}(r)$, where $\sqrt{3}F^{(2)}(r)$ indicates the three-body force while neglecting the many-body effect. Figure 1 shows that both the two-body force $F^{(2)}(r)$ and the three-body force $F^{(3)}(r)$ decay slowly as a function of distance r. In addition, the inset shows that the triplet force $\Delta F(r)$ becomes repulsive among charged dendrimer molecules. It is shown that the characteristics of triplet force in this system are repulsive, indicating the importance of the nonlinear feature due to the excluded volume effect incorporated with the screened Coulomb effect on charged dendrimer monomers.

These results demonstrate that the contribution by Coulomb effect and the excluded-volume effect are deeply related and cannot be treated independently. These studies shed light on the characteristic features of soft colloidal system, indicating that the structural formation of the self-assembly of charged dendrimers in dense solution may quite differ from those of hard-sphere suspensions. It will also motivate the development of novel, potential applications such as encapsulation of guest molecules, and self-assembly of soft colloids such as nano-colloidal crystals.

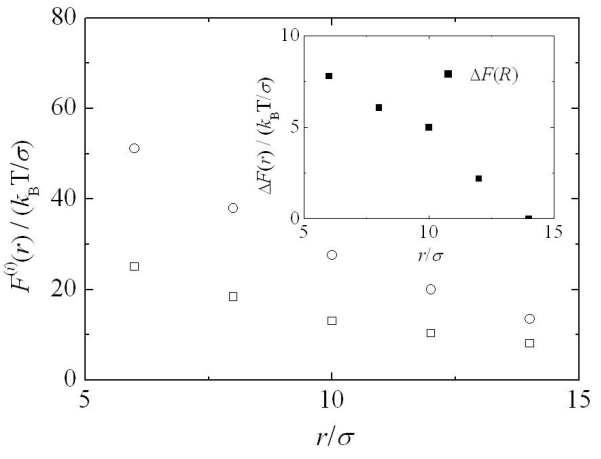

Fig. 1 Effective forces $F^{(i)}(r)$ $(i = 2,3)$ among charged dendrimers. The inset shows the profile of the triplet force $\Delta F(r) \equiv F^{(3)}(r) - \sqrt{3}F^{(2)}(r)$.

References

[1] T. Terao, Phys. Rev. E **66**(2002) 046707.