Statistical Mechanics Study of Strong Attraction between Like-Charged Particles in an Electrolyte Solution

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Negatively charged particles repel each other in a vacuum. However, they are not necessarily repulsive under any conditions. The effective attraction between like-charged particles has been observed in an electrolyte solution. Zhang et al. showed the effective attraction experimentally and indicated important progress regarding the ion-specific effects on proteins [1-3]. The results go beyond generic Hofmeister interactions. In their experiments, the like-charged particles were acidic proteins which were negatively charged particles, and the electrolyte solution had multivalent cations, such as Y3+. The effective attraction appeared only under certain electrolyte concentrations. So, the electrolyte concentration dependence of the interaction showed a reentrant behavior. In a dilute electrolyte concentration, the effective interaction was repulsive. And the strong attraction appeared when the concentration became higher. However, the strong attraction disappeared if they added more electrolytes to the solution. The effective attraction and the reentrant behaviors are not only interesting in the phase behaviors of the protein solution but also important properties in the crystallization of protein.

We calculated the effective interaction between like-charged particles using the integral equation theory, such as the HNC-OZ equations[4]. The numerical solutions showed the reentrant behavior when the Coulomb interaction was dominant. The correlation functions suggested that the cations mediated the effective attraction between negatively charged particles. When the cations localize at mediation site A (See Fig. 1), the cations attract negatively charged particles. The small anions are excluded from site A due to the direct Coulomb repulsion. Thus, the effective interaction depends on the local density of the cation at site A. The effective interaction becomes attractive when the total attractive interaction becomes larger than the repulsive interaction between the negatively charged particles. We confirmed this story of the reentrant behavior based on the correlation functions obtained by the integral equation theory.

The strong attraction and the reentrant behavior have been explained based on the Coulomb interaction. On the other hand, solvent granularity strongly assists the behaviors[5]. We examined explicit and implicit solvent models. The calculated results indicated that the solvent granularity enhanced the effective attraction, and the reentrant behavior became clearer. This assistance is not a simple depletion force between macroanions. We analyzed this enhancement mechanism based on the calculated correlation functions. The results showed that the depletion force induced by the solvent granularity enhanced the effective attraction between a macroanion and a cation. However, the enhancement is not significant. Indeed, the increased amount is almost similar to that of the uncharged system, and we can estimate the increase using the Asakura-Oosawa theory. However, this minor enhancement leads to the significant enhancement of the effective attraction between macroanions because of the minor increase of local density as site A, namely the mediation site of the effective attraction.

We also studied the effects of cation exchange[6] and ionic sizes[7] using the HNC-OZ theory. And we discussed the phase diagrams [8]. We are also calculating the effective interaction using

molecular simulations. In this presentation, we will review these results. And we will discuss the effect of solvent granularity and some new results.

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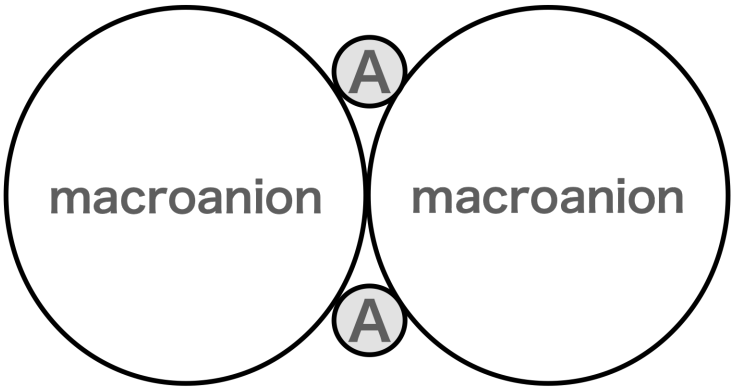

Figure 1: Schematic diagram illustrating the association of two macroanions. The cations are localized at site A due to the Coulomb interaction. The macroanions effectively attract each other when the attraction mediated by the cations is stronger than the direct Coulomb repulsion between the macroanions. This is similar to a classical picture of the covalent bond.