Depletion Layer near a Wall in Polyelectrolyte Solutions

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中性のコロイド粒子を高分子溶液に分散させた系では、粒子間に働く力として、枯渇凝集力が知られている。この力は、コロイド粒子のまわりに高分子の枯渇層が生じることによる浸透圧の効果である。本研究では、この高分子溶液が高分子電解質である場合のコロイド粒子表面近傍の高分子の濃度プロファイルを論じる。添加塩が無い場合、高分子中のイオンの解離度が大きくなるにつれて、枯渇層の厚さが減少する。また、中性の高分子の濃度プロファイルとは違って、枯渇層端での逆にに高分子の濃度の濃い領域が存在することが分かった。これは、枯渇層末端での電気二重層の形成によるものである。

It has been well known that an addition of a small amount of neutral polymers to colloidal suspensions yields an attractive interaction between particles. The attractive interaction comes from the depletion layer of polymers near the colloidal particles [1]. In many food and biological colloidal systems, water soluble polymers are polyelectrolytes. However the interaction between neutral colloidal particles in polyelectrolyte solutions has not been explored in depth yet. Therefore, it is quite important to know the detail profile of polyelectrolyte concentration near a colloidal particle. In this work, we focus on the concentration profile of polyelectrolytes near a neutral colloidal particle.

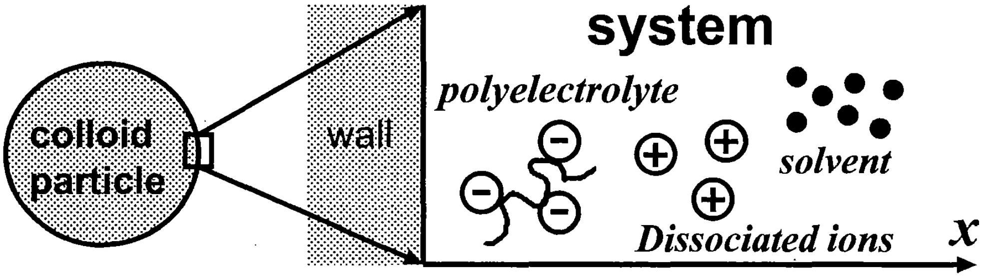

Figure 1: Schematic view of the system that we consider in this work.

Now we consider a polyelectrolyte solution near a neutral colloidal particle as shown in Fig. 1. The solution is composed of a solvent, polymers having negative charges and dissociated positive counter ions from polymers. Since we consider a following situation that the polymer concentration C ($= \phi_p/a^3$, ϕ_p and a being the volume fraction of polymer and the monomer size) is much lower than overlap concentration C^*, ($C \ll C^*$) and the gyration radius of polymer chain R_G is much less than the radius R of a neutral colloidal particle ($R_G \ll R$), the surface of colloidal particle can be regarded as a flat neutral wall for a polymer chain. In our modeling of polyelectrolyte, each monomer of polymer carries a fraction p of a charge e. In order to investigate statistical properties of such a polyelectrolyte solution, self-consistent field theory (SCFT) is quite effective. The details of the equations and calculation method can be seen in the paper by Q. Wang [2].

By using the SCFT method, we calculated the concentration profile of polymer segment in polyelectrolyte solution near a neutral flat wall. In Fig.2(a), we show a concentration profile in a typical polyelectrolyte solution system where the bulk concentration ϕ_b is 1.0×10^{-5}, $N = 1000$ and $\tau = \ell_{\mathrm{B}}/a = 1$, ℓ_{B} being the Bjerrum length. We found that the depletion thickness δ_{PE} decreases as the degree of dissociation p becomes larger. In addition to this, the profile of concentration for higher values of p has a small hillock at the end of depletion layer. The hill of the concentration originates from the formation of electric bilayer at the end of depletion layer, see Fig.2.

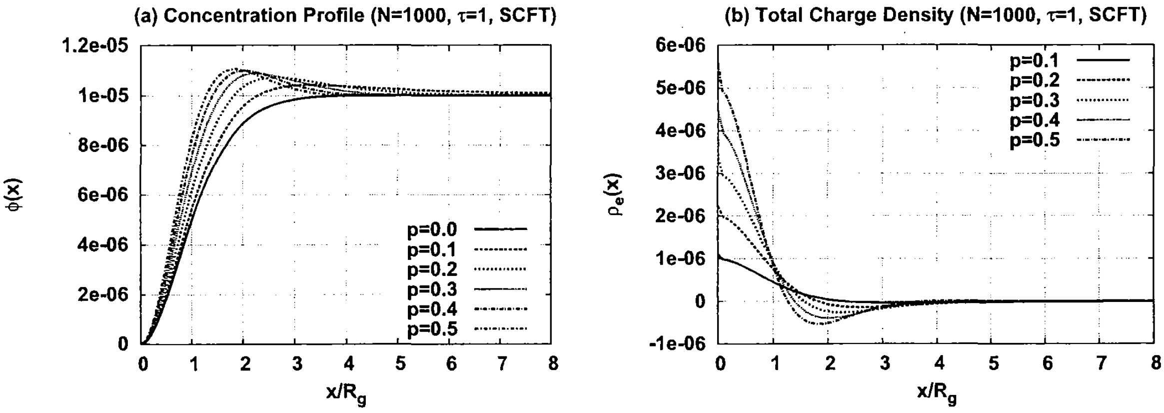

Figure 2: (a) Concentration profiles and (b) Total charge density profile for degree of dissociation of ion from a polymer chain $p = 0.0,\ 0.1,\ 0.2,\ 0.3,\ 0.4,\ 0.5$.

References

[1] S. Asakura and F. Oosawa, *J. Chem. Phys.* **22** (1954), 1255.

[2] Q. Wang, T. Taniguchi and G. H. Fredrickson, *J. Phys. Chem. B*, **108** (2004), 6733.