# Complex Fluids에 대한 분자시뮬레이션 기법 연구(I) : 임의의 농도를 갖는 콜로이드 서스펜션의 거동

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# Study on the molecular simulation for complex fluids(I) : the behavior of colloidal suspension with arbitrary concentrations

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## Introduction

Complexity and flexibility due to their unique molecular and supermolecular structures, which are not shown in ordinary condensed phases, characterize the complex fluids. The fundamental research regarding it dynamics and structural behavior is provided so as to understand its physicochemical aspect[1]. The colloidal suspensions confined with solid walls are a frequently encountered situation, including membrane pore, polymeric gel, and many kinds of porous media[2]. However, note that most of studies have been contributed to the colloids in unbounded spaces.

Currently, it is obvious that the complex fluids system is examined by employing the molecular simulations. In this research, we address the simulation results for concentrated colloidal suspensions obtained by a Gibbs ensemble Monte Carlo(GEMC) scheme. Exciting challenges are ahead in systematic analyses on the density profile, the concentration partitioning, and the orientational order.

## Stochastic Gibbs ensemble Monte Carlo for colloidal suspensions

With probability distribution $p$, a general Monte Carlo simulation would sample the Boltzmann distribution

$$p(\underline{r}_1, \cdots, \underline{r}_N) = \exp[-E(\underline{r}^N)/kT]/\Xi \quad (1)$$

where $\underline{r}^N$ is molecular configuration, $\Xi$ is the configurational partition function, and $kT$ is the Boltzmann thermal energy. The fundamental insights and research progress in the statistical mechanics incorporated Monte Carlo technique can be found in relevant articles[3,4].

The GEMC method was originally used with considerable success to study problems of phase equilibria. The Gibbs ensemble consists of the elements of canonical ($NVT$), isobaric-isothermal ($NPT$), and grand canonical ($\mu VT$) ensembles. With consisting of a solid pore and a bulk, the exchanges of volume between two regions do not need to include coexisting subsystems. Therefore, both particle displacement and interchange moves are performed in the computational cycle of current GEMC simulations[5].

Fig. 1 shows the periodic unit cells, where the respective periodic

boundary conditions are imposed for the axial direction in the pore and all directions in the bulk. States in the canonical ensemble of the *NVT* Metropolis process occur with a probability proportional to $\exp(-E^{\alpha}/kT)$ for an arbitrary subsystem. The new configurations in the *NVT* process are generated with a probability $p_D$ given by

$$p_D = \min\left[1,\ \exp\left(-\Delta E^{\alpha}/kT\right)\right] \tag{2}$$

where $\triangle E$ represents the change in interaction energy caused by the move. In the $\mu VT$ process, the probability governing the particle transfer from subsystem $\alpha$ to subsystem $\beta$ is provided as

$$p_T = \min\left[1,\ \exp\left\{-\left(\frac{\Delta E^{\alpha}+\Delta E^{\beta}}{kT}\right)+\ln\left(\frac{N^{\alpha}V^{\beta}}{(N^{\beta}+1)\ V^{\alpha}}\right)\right\}\right] . \tag{3}$$

Therefore, the particle positions are generated stochastically such that a configuration depends necessarily on the previous configuration.

**Modeling results**

1. *spherical colloids* : The concentration profile of solutes is determined from monitoring of the density profile. The density profile in the bulk shown in Fig. 2 can be considered in terms of the radial distribution function. This indicates how, on average, particles are distributed around an arbitrarily chosen reference sphere. It is clearly seen that the density is zero when the distance is less than the sphere diameter, and far from a test particle the density profile is uniform. This feature can be identified in the result previously reported. Compared to a regularly increasing function at low concentrations, concentrated systems exhibit damped oscillations, the maxima of which occur near multiples of the nearest-neighbor distance.

We can see the radial density profiles of a cylindrical pore. The stochastic fact that the solute density is relatively high near the inert pore wall is typical in equilibrium partitioning of uncharged case. When the solute concentration $C_b$ is increased to 20% from 5%, the density profile becomes more oscillated. The density profiles from the GEMC are compared with corresponding predictions from the virial expansions, and agree well entirely at a solute concentration of 5%. The discrepancy between the two methods is shown at 20%.

2. *non-spherical colloids* : Compared to the spherical colloids, the MC simulations for non-spherical colloids are more complicated due to an anisotropic effect. A desired spheroid has been generated with the effective location of element spheres inside a domain shown in Fig. 3, which provides a reduction of computation time. Further, a triple of Eulerian angles should be applied to describe arbitrarily the spheroid configurations. Two density profiles based on a monomer and a center-of-mass can be estimated as given in Fig. 4. Also, the orientational order can be determined.

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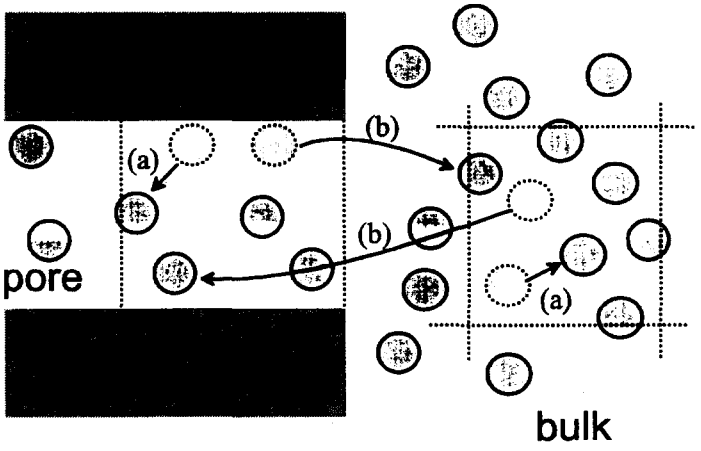


Fig. 1. GEMC method for the simulation of equilibrium partitioning; (a) random displacements, (b) particle interchange between two regions.

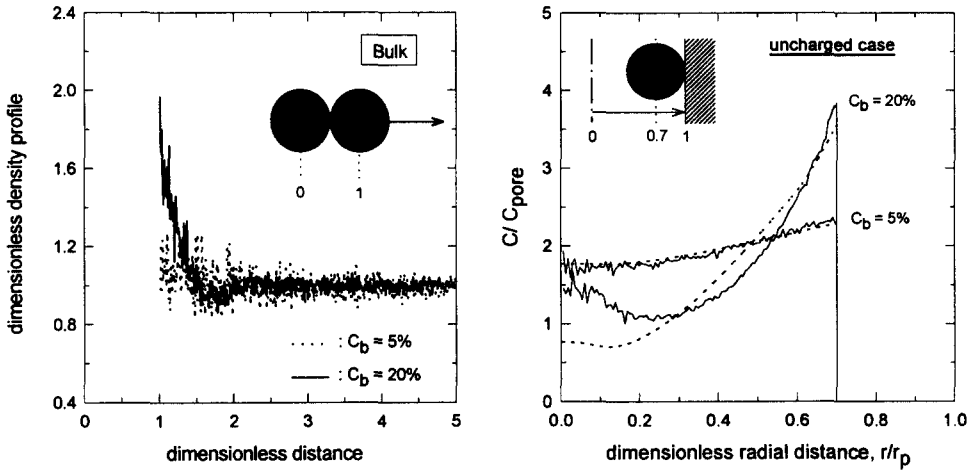


Fig. 2. Density profiles of inert solutes in a bulk (left) and a cylindrical pore (right) for $\lambda$ = 0.3 and solute concentrations of 5 and 20 vol%. Dotted curves correspond to virial expansion results.

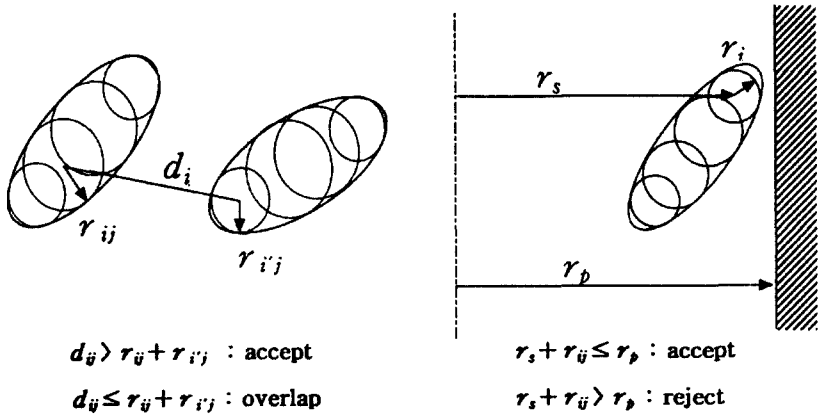


Fig. 3. Illustrations of the overlap test with pair-interaction.

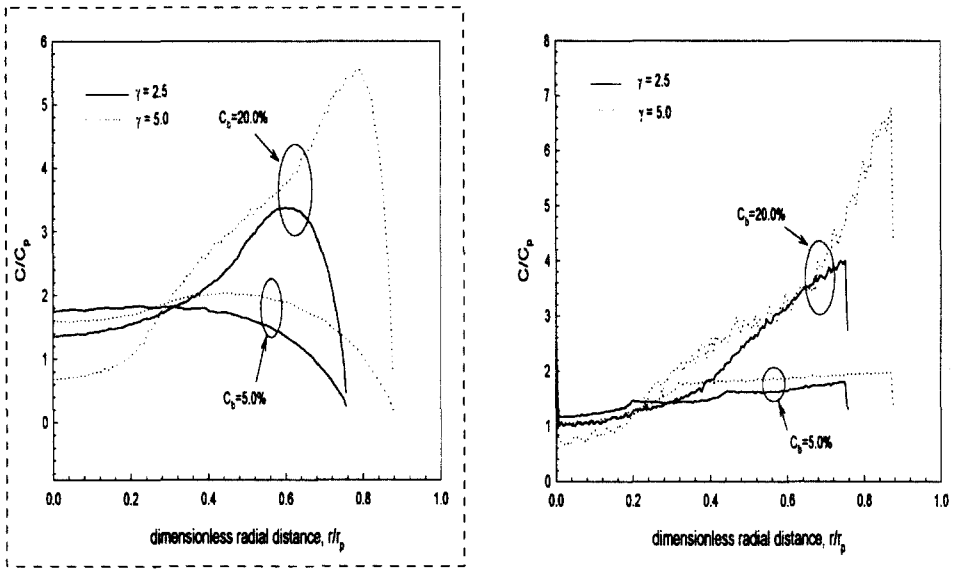


Fig. 4. The profiles of monomer density (left) and center-of-mass density (right) of inert spheroidal colloids in a cylindrical pore for aspect ratios of 2.5 and 5.0, and solute concentrations of 5 and 20 vol%.