Reversible and Hierarchical Coarse-grained Particle Model and Dynamics Simulation Method for Complex fluids

(可逆階層的粗視化粒子モデルと複雑流体のための動力学計算手法)

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Introduction

Ordered phases of soft-matters and dynamic properties of complex fluids have attracted intensive scientific interest, and well-controlled meso-scale architectures of such materials are potentially suitable for a large number of novel technological applications. In terms of numerical simulations, the enormous length-scale and time-scale of such systems are far beyond the range of atomistic molecular simulations (MD). On the other hand, molecular structure and their interactions are still playing important roles in such length-scale, and these are too complex and beyond the scope of macroscopic fluid dynamics (FD).

Dissipative particle dynamics (DPD) has been introduced as a simulation method for study of hydrodynamics behavior [1], and its combinations with the bead-and-spring model seem very promising for simulations of structure and dynamics of soft-matters [2]. DPD is mainly based on simulations of particles with soft-repulsive interactions, and pair-wised dissipative-and-random forces. The dissipative-and-random forces enhanced the collisions among particles, which implicitly represent its internal degree of freedoms, and the thermal-fluctuation ensured it to simulate a Hamiltonian system in canonical ensemble. The soft-particles represent a group of molecules or segments, and in principle, it allows a much larger time-step than MD simulations with the bead-and-spring model. A fundamental problem of DPD is that the coarse-graining procedure is not clear, namely the use of the "soft-repulsive" model in DPD simulation results in a loss of connections to the phase behavior of the underlying molecular systems. In particular, the "soft-repulsive" model is inadequate for studies of complex fluids that are critically depend on the balance of attractive-and-repulsive forces among the particles.

In this work, we first defined three essential coarse-graining procedures: (G) Grouping, (P) Packing, and (T) Time-averaging, as schematically illustrated in Fig.1. Grouping is essentially an extension of unit-atom to a larger scale, packing is in fact grouping of solvents or small molecules, and time-averaging is considering the effective potential between two groups of particles over a finite time-span. The results of Forrest and Suter[3] have clearly shown that a model based on the Lennard-Jones (LJ) potential is not suitable for time-coarse-graining.

To adopt all these procedures and construct particle models for soft-matters, we then devised a "soft-attractive-and-repulsive" potential model, which has adjustable hardness parameter (denoted as β) and cut-off range. The resulting "attractive-and-repulsive" models are capable of reproducing thermodynamics properties and liquid-vapor coexistence curves of real fluids at atomic scale (a model with β=6 is very similar to that of LJ model) and various time-coarse-

grained levels (when $\beta<6$). Fig.2 shows the liquid-vapor coexistence curves of short range interacting models, and we found that the resulting curves are in good agreement with LJ model for models with $\beta=5$ to 3. For the model with $\beta=3$, which analytically represents the effective potential over a long time-span, the new potential has a relatively smooth-and-soft function. As a result, it gives excellent total-energy-conservation in NVE MD run with a very long time-step in reduced-unit, in comparison with MD of LJ model.

Practically, the "soft-attractive-and-repulsive" coarse-grained model could be combined with any particle simulation method. Combining the new model with DPD, however, will enable us to parameterize the dynamics properties and to take account of the thermal-fluctuations of the coarse-grained particles without losing the static thermodynamics properties and phase behavior of the under-laying molecular systems.

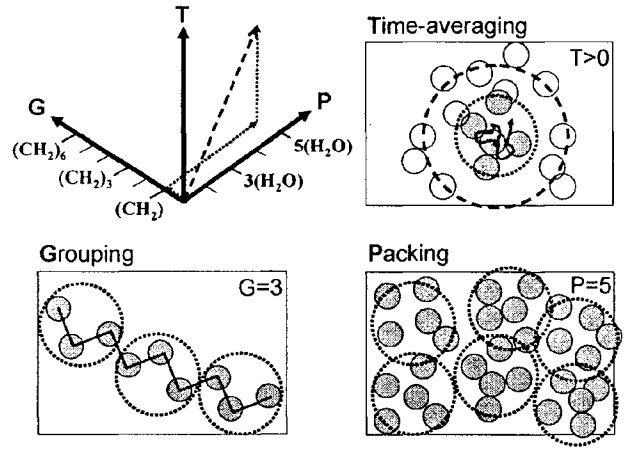

Fig. 1. Schematic illustration of the essential coarse-graining procedures.

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Reference

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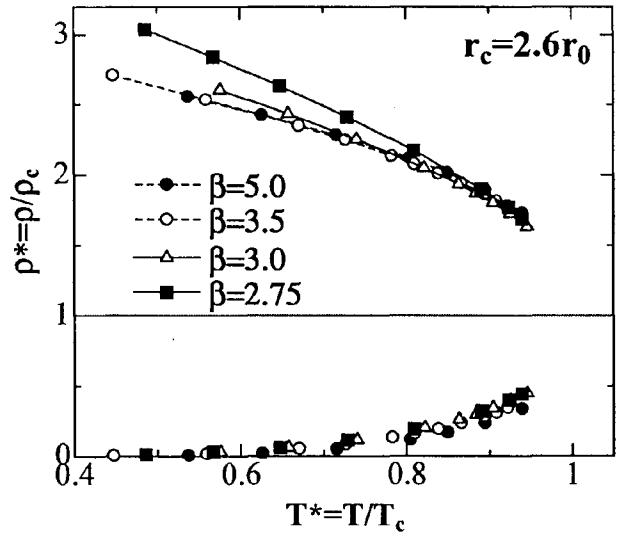

Fig.2. Liquid-Vapor envelops in reduced-unit obtained by Gibbs ensemble for the new coarse-grained model with an adjustable hardness parameter, β.