A Space-Time Coarse-Grained Model for Particle Simulations of Soft Matter

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ABSTRACT

We have devised a simple soft-attractive-and-repulsive pair-potential model, which has a hardness parameter (β) and a smooth cut-off, to adopt coarse-graining procedures for soft-matter. Namely, (i) Grouping for a monomer or segment of molecules; (ii) Packing for a group of molecules; and (iii) Time-averaging to take account of effective potential, $U_{eff}(r)$, over a time-span. The resulting models are capable of reproducing liquid-vapor coexistence curves of real fluids at various space-time coarse-grained levels. A model with β=3.0 is analytically representing a time-averaged $U_{eff}(r)$ over a long time-span, gives excellent energy conservation with a very long time-step. Combining the new model with dissipative particle dynamics (DPD) method should allows us to retain the phase behavior and dynamics properties of underlying molecular systems. In this work, we have performed DPD simulations of surface-induced nano-pattern of block copolymer film, and found that the simulated surface structures resembled those patterns observed in experiment of symmetric PS-b-PMMA thin films on a PS-coated substrate.

Keywords: nano-pattern, block copolymer, thin film, coarse-grained model, dissipative particle dynamics.

1 INTRODUCTION

Ordering of colloidal particles and well-controlled structures of soft matter are potentially suitable for a large number of nano-scale technological applications. The enormous length-scale and time-scale of such systems, however, are far beyond the range of atomistic molecular simulations (MD). On the other hand, molecular structure and their interactions still play important roles in such length-scale, and these are too complex for macroscopic fluid dynamics (FD). From this viewpoint, dissipative particle dynamics (DPD) method seems to be promising for simulations of such meso-scale systems [1,2].

In brief, DPD is based on simulations of particles with "soft-repulsive" and dissipative-and-random forces. The dissipative-and-random forces enhanced the collisions among particles, implicitly represent the internal degrees of freedom of coarse-grained particles, and hence effectively stretched the characteristic time-scale of the simulated system. More importantly, the fluctuation-and-dissipation relation ensures that DPD is simulating a Hamiltonian system in canonical ensemble [3]. Furthermore, the soft-particles represent a group of molecules or segments, and it allows a much larger time-step than molecular dynamic (MD) method. A fundamental problem of DPD, however, is that there is no straightforward procedure to derive the soft-particle model from a realistic molecular model. 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. Practically, it is impossible for simulation of soft-matter at free surface.

To overcome this problem, we have developed a series of particle models that are consistent in phase behavior at various space-time coarse-grained levels [4]. Here, as a demonstration, we have combined the new model with DPD for simulations of surface-induced nano-pattern of block copolymer thin film. Using a simple model for block copolymer, we found that the simulated structure resembled those patterns observed in experiment of symmetric PS-b-PMMA thin films on a PS-coated substrate.

2 COARSE-GRAINED MODEL

It will be useful to divide essential coarse-graining procedures into (i) Grouping, (ii) Packing, and (iii) Time-averaging, as schematically illustrated in Fig.1.

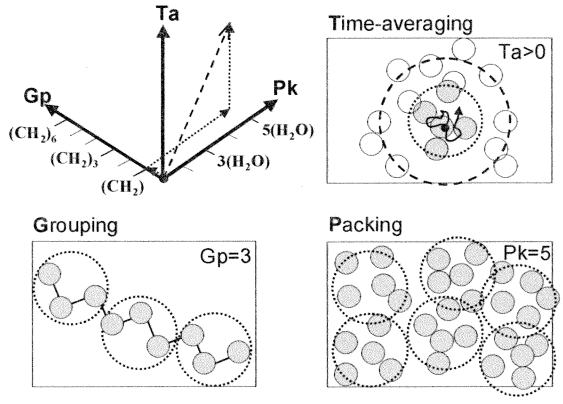

Figure 1: Schematic illustrations of the three essential coarse-graining procedures for soft matter.

Grouping (Gp) can be considered as an extension of united-atom to a larger scale for monomer or segment in different coarse-grain level for a large molecule, such as $(CH_2)_3$ and $(CH_2)_6$ for n-alkanes. In practice, all parameters

for the inter-molecular and intra-molecular potentials will have to be re-parameterized to represent a larger group.

Packing (Pk) is meant to represent the effective potential ($U_{eff}(r)$) for a group of solvent or small molecules that are loosely gathering. This is, in fact, the original concept for the "fluid particles" in DPD; however, we required that they are consistent in phase behavior. We have shown in our recent work [4], that the model from a smaller group can be adopted by simply scaling the length parameter to represent a larger group.

Time-averaging (Ta) is meant to consider the $U_{eff}(r)$ between two groups of particles over a finite time-span. Forrest and Suter [5] have performed a MD simulation of polymer melts using LJ(12-6) based united-atom chains, and they found that the $U_{eff}(r)$ pre-averaged over a long time-span are much softer and shallower than the original potential. They have clearly shown that LJ potential is not suitable to represent a time-coarse-grained potential. However, they did not derive an analytical function from their tabulated $U_{eff}(r)$.

To adopt all these procedures, we have devised a "soft-attractive-and-repulsive" potential model [4], which has an adjustable hardness parameter (β) and a smooth cut-off (r_{cut}). The potential can be written as a combination of a Morse-like function with a damping function, $w(r_{ij})$, to give a smooth cut-off and limit the interaction range,

$$U(r_{ij}) = \varepsilon\left\{\left(1-\exp\left[-\beta\left(r_{ij}/r_{\min}-1\right)\right]\right)^2 - 1\right\} w(r_{ij}) \qquad (1)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, and ε determines the depth of the potential minimum which is located at r_{min}. The damping function can be written as

$$w(r_{ij}) = \begin{cases} 1.0 & for \quad r_{ij} < r_{\min} \\ \left[1-\left(\dfrac{r_{ij}-r_{\min}}{r_{cut}-r_{\min}}\right)^n\right]^n & for \quad r_{\min} \le r_{ij} \le r_{cut} \\ 0.0 & for \quad r_{ij} > r_{cut} \end{cases} \qquad (2)$$

where n is a small integer. We found that n=2~4 gives smooth functions at the cut-off region and does not strongly alter the features of the Morse force functions. We are using n=2 in this work. Note that β is a dimensionless parameter, and when β=6, the function is very similar to LJ(12-6) model. Thus, it could be adopted for Gp procedure, as well as for atomistic model.

The distance at $U(r_{ij})$=0, denoted by r_0, is defined as the reduced unit of length; its relation with r_{min} and β can be written as $r_0 = r_{min}(1-\ln 2/\beta)$. We take ε as the reduced unit of energy, so for a particle with mass, m, the time-scale is $t_{sc}=r_0(m/\varepsilon)^{1/2}$ and the reduced time is $t^*=t/t_{sc}$. When we set $\varepsilon=1$, $r_0=1$ and $r_{cut}=2.6r_0$, the liquid-vapor coexistence curves of the model with β=5.0~3.0 are in good agreement with LJ(12-6) model, as shown in Fig.2.

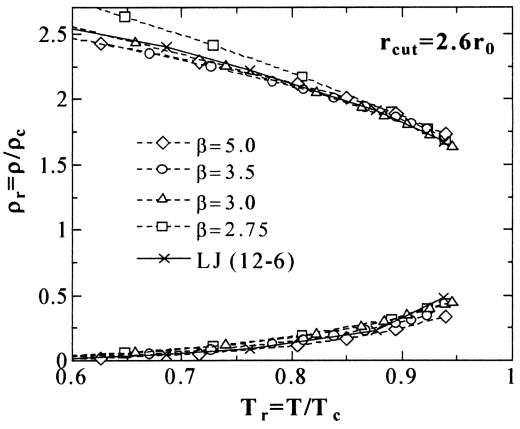

Figure 2: Liquid-Vapor envelops obtained via Gibbs ensemble Monte Carlo method for models of β=5.0~2.75 in comparison to that of LJ (12-6) form ref. [6,7].

The functions of models with ε and r_0 being adjusted to give the similar critical point as that of β=5.0, shown in Fig.3, strongly resembled those time-coarse-grained $U_{eff}(r)$ of Forrest and Suter [5]. This is not enough to justify, but it indicates that a model with β<5.0 could analytically represent time-coarse-grained $U_{eff}(r)$ at longer time-spans. A clear difference is that the tabulated $U_{eff}(r)$ of ref.[5] were obtained by time-averaging at a specific temperature and density, while our potential models reproduce the phase behavior at full temperature range.

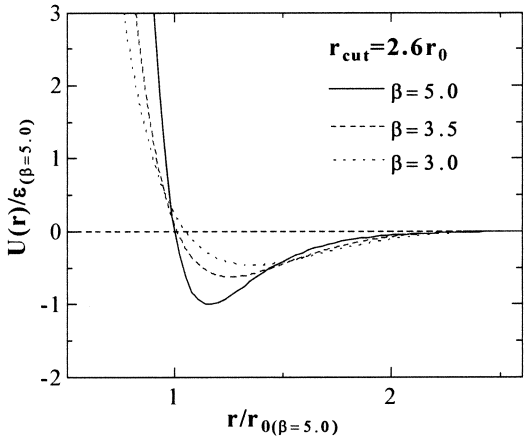

Figure 3: Potential functions of models with β=5.0 to 3.0 that give similar critical temperature and density.

Considering a model of β=3.0 as an analytical function of $U_{eff}(r)$ over a long time-span for a model with β=5.0, is in accord with the fact that t_{sc} of β=3.0 is larger than that of β=5.0, since ε of β=3.0 is about a half of that of β=5.0. Furthermore, since the model of β=3.0 has a very smooth-and-soft function, it gives excellent energy-conservation in NVE-MD run with a very long time-step (Δt^*=0.02) in comparison to that of LJ model (Δt^*=0.004).

3 COMBINATON WITH DPD METHOD

The "soft-attractive-and-repulsive" model can be combined with any particle simulation method, such as MD, hybrid Monte Carlo, or Brownian Dynamics. Combining the model with dissipative-and-random forces of DPD will enable us to retain the dynamics properties of the particles for large-scale simulations of soft-matter.

The dissipative-and-random forces of DPD are given by

$$F^D(r_{ij}) = -\gamma\, w^D(r_{ij})\,(\mathbf{v}_{ij}\cdot\mathbf{r}_{ij})\,\mathbf{r}_{ij}/r_{ij}^2 \tag{3}$$

$$F^R(r_{ij}) = \sigma\, w^R(r_{ij})\,\xi_{ij}\,\mathbf{r}_{ij}/r_{ij} \tag{4}$$

where $\mathbf{v}_{ij}=\mathbf{v}_i-\mathbf{v}_j$; ξ_{ij} is an independent random number with Gaussian statistic for each pair of particle; $w^D(r_{ij})$ and $w^R(r_{ij})$ are weight functions that are related to each other, and the friction and random amplitudes, namely γ and σ, are related to k_BT:

$$w^D(r_{ij}) = [w^R(r_{ij})]^2 \quad ; \quad \sigma^2 = 2\gamma k_B T \tag{5}$$

For our new model, we defined

$$w^D(r_{ij}) = \begin{cases} (1-r_{ij}/r_d)^2 & for \quad r_{ij} < r_d \\ 0 & for \quad r_{ij} \ge r_d \end{cases} \tag{6}$$

where the forces are vanishing at r_d, a range in between r_{min} and r_{cut}, and we have shown that it can be used as a parameter to adjust and hence retained the dynamics properties of a coarse-grained model particle [4].

4 MODEL OF BLOCK COPOLYMER

For polymer systems, monomers are threaded together in linear chains, using the harmonic bond stretching (U^{bond}), and bond-angle (U^{angle}) interactions:

$$U^{bond} = K_b(r-r_{eq})^2 \tag{7}$$

$$U^{angle} = K_a(\theta-\theta_{eq})^2 \tag{8}$$

where r is the bond length and θ is the bond angle. The parameters $r_{eq}=r_0$, $\theta_{eq}=\pi/2$, $K_b/\varepsilon=200$ and $K_a/\varepsilon=10$ were employed in this work. As space is limited, detailed modeling of polymers using this model will be presented in another paper.

Model of polymer can be related to the Flory-Huggins χ-parameter. For polymer of two components, A and B, that do not favor contact, the χ-parameter can be obtained via observation of polymer segregation, as have been done in ref.[2] using the following equation

$$\chi N = \frac{\ln[(1-\phi_A)/\phi_A]}{1-2\phi_A} \tag{9}$$

where ϕ_A is the volume fractions of the A component, and N is the polymer length.

A mixture of homo-polymers of $N=N_A=N_B$ is modeled by using particle model of β=3.0 with $\varepsilon=1.0$, $r_0=1.0$ for both monomer of A and B. In this work, however, we are limiting the non-bonded particle interactions to a shorter range by $r_{cut}=2.0r_0$, and we defined the A-B interaction as

$$\varepsilon_{AB} = (1-\Delta)\sqrt{\varepsilon_{AA}\varepsilon_{BB}} \tag{10}$$

where Δ is a parameter to adjust the affinity of A-B monomers. Fig.4 shows the results for polymers at monomer density $\rho^*=\rho/r_0^{-3}=0.8$ and $T^*=k_BT/\varepsilon$=2.0.

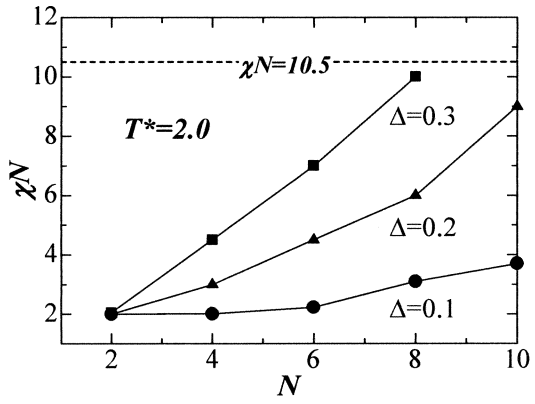

Figure 4: χN vs. N for mixture of homo-polymers with $N=N_A=N_B$ and various A-B affinity Δ-parameters.

It is known that the phase separation or order-disorder transition (ODT) of symmetric block copolymer in bulk system occurs when $\chi N>10.5$, see ref.[8]. For our model with $\Delta=0.2$ and $N=10$, we estimated $\chi N=9$ (see Fig.4). For the following section, a symmetric block copolymer of $N=10$ ($N_A=N_B=5$) with $\varepsilon=1.0$, $r_0=1.0$ for both component A and B is adopted. Samples of copolymer firm at $T>T_{ODT}$, the firm were generated using A-B affinity of $\Delta=0.1$ or 0.2. While for copolymer firm at $T<T_{ODT}$, the A-B affinity parameter of $\Delta=0.3$ or higher value was employed.

5 NANO-PATTERN OF BLOCK COPOLYMER

We have performed DPD simulations of surface-induced nano-pattern of block copolymer film. A layer of polymer substrate (=A) is fixed at the bottom of the simulation box using a harmonic spring, and temperature at $T^*=k_BT/\varepsilon$=2.0. The CPU time requirement for a long simulation of $t^*=30\times10^3$, as for fig.5, was about one hour on a 600MHz Alpha-ev6 processor using Δt^*=0.02.

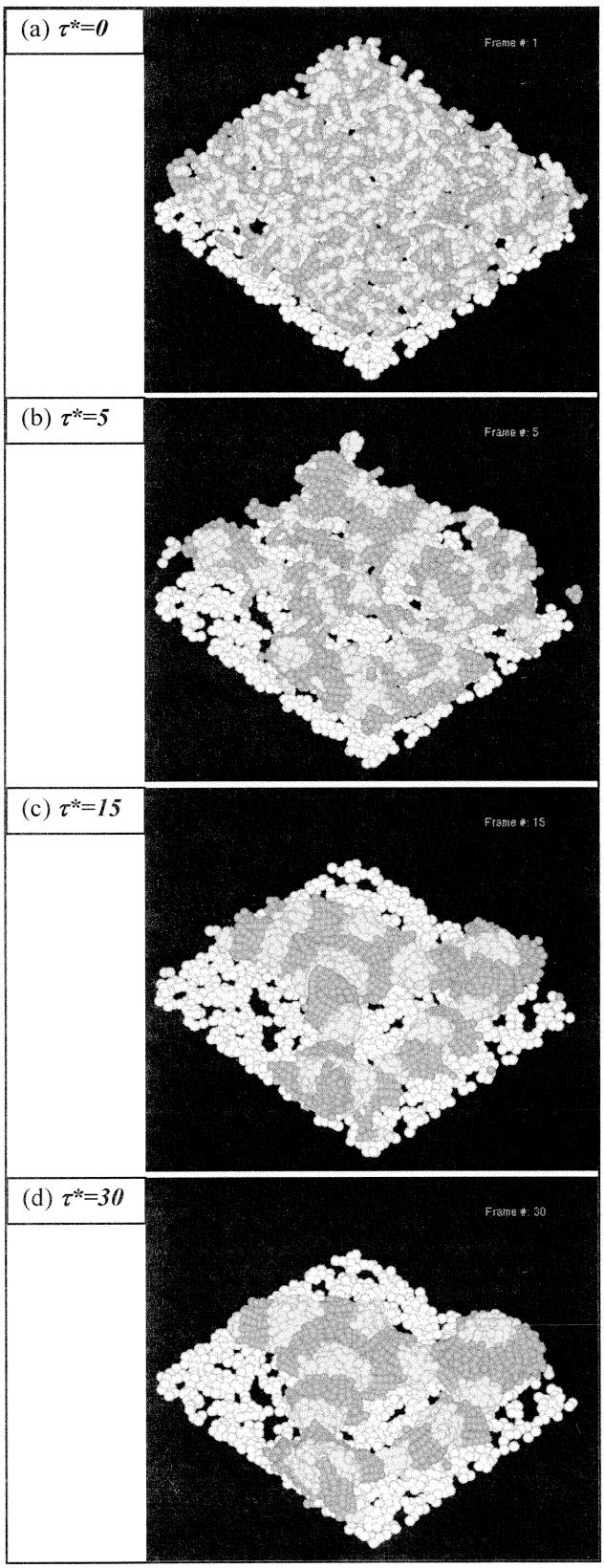

Figure 5: Snap-shots ($\tau^*=10^3 t^*$) of DPD simulation for diblock copolymer (A_5-B_5: dark gray-pale gray) thin film of $\Delta=0.5$ on a polymer substrate (A: white) at $T^*=2.0$.

We found that the simulated pattern of a sample of $\Delta=0.5$, a "bicontinuous" pattern as shown in Fig.5(d), resembled those observed in experiment of symmetric block copolymer thin film at $T<T_{ODT}$ [8]. While some other simulated patterns using $\Delta=0.2$, resembled those observed in experiment of symmetric PS-b-PMMA copolymer thin film (initial thickness h<3.5nm) on a PS-coated SiO_x substrate at $T>T_{ODT}$ [8,9].

In conclusion, we have developed a "soft-attractive-and-repulsive" model for particle dynamics simulation of soft matter. In particular, a model with β=3.0 is analytically representing the effective potential time-averaged over a long time-span, and allowing particle simulation using very long time-step. We have shown that the combination of the new model with the DPD method allows us to reproduce experimental observed nano-patterns at below and above the ODT regime of symmetric block copolymer thin films.

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