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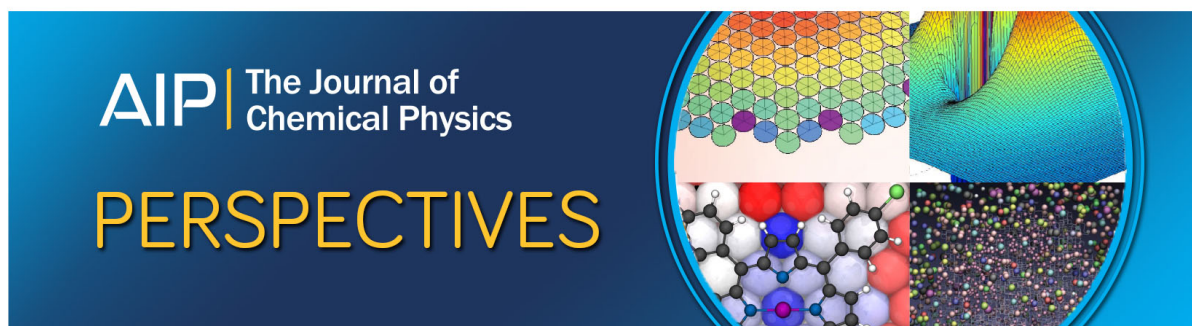
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# Self-assembly of the symmetric diblock copolymer in a confined state: Monte Carlo simulation

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Self-assembly of symmetric diblock copolymers in confined state has been investigated by means of Monte Carlo simulation method. The symmetric diblock copolymers were confined in two- (parallel walls or circle) or in three-dimensional (spherical or cylindrical) space. There are interactions between these boundaries and the symmetric diblock polymers. These interactions and boundary shape resulted in the formation of novel self-assemble structures, e.g., strip, circle, core-multishell, and multibarrel-layer structures. Simulation results predicated that it is possible to design different phase structures for block copolymers by adjusting boundary shape and boundary-block copolymer interactions. © 2001 American Institute of Physics. [DOI: 10.1063/1.1372189]

## INTRODUCTION

The design of polymer materials with novel phase structures, such as self-assembly ones, has become of great interest and importance in scientific and technological views. The polymer materials with novel phase structure should have special physical properties and applications.<sup>1</sup> Recently, special phase behaviors of block polymers confined into two parallel walls have received more attention.<sup>1–8</sup> It is possible to obtain novel phase structures for block copolymers by designing boundary conditions for a special purpose.<sup>3</sup> If block polymers are confined between two parallel walls in which there are interactions between the wall and block copolymers, this will result in the performance of the strip structure for the confined block copolymers.<sup>1,3,8</sup> Lambooy *et al.*<sup>9</sup> have investigated polystyrene-poly(methyl methacrylate) diblock copolymers confined into silicon wafers. Oriented lamella morphology has been found in which the numbers of internal interfaces increase with the increase of the film thickness. To our knowledge, most researchers have focused on the phase behaviors of block copolymers, which are confined between parallel walls.<sup>10</sup> However, in fact due to special applications, one needs to design different morphologies, such as circle circuits and spherical optical devices. It is believed that the design of novel morphology with special properties and functions in various application fields is necessary.<sup>1,3</sup>

Computer simulation methods play a great role in polymer science.<sup>11</sup> Simulation results can complement and validate theoretical predictions. More importantly, they could

provide useful insights for future experimental work. In this paper, we reported the computer simulation results of self-assemble behavior for symmetric diblock copolymers in a confined state in which there are interactions between the boundary and the diblock copolymers.

## MODEL AND SIMULATION

Monte Carlo simulation of the phase structure for symmetric diblock copolymers was performed in two and three dimensions with various boundary shapes in which there are interactions between the boundary and the diblock copolymers. The two- or three-dimensional space is filled with A–B symmetric diblock polymers. The diblock copolymer has 10 units in A block and 10 units in B block. The 90% lattice sites in the case of two dimensions, and 70% lattice sites for three dimensions are occupied by the diblock copolymer. Periodic boundary conditions were imposed in the  $L_x$  direction for parallel-wall boundary in 2D and barrel boundary in 3D shown in Figs. 1 and 2. There are attractive interactions between the boundary and A block and repulsive interactions of the boundary with the B block. The single-site bond fluctuation model<sup>12–14</sup> was used in this Monte Carlo simulation. The evolution of the chain configuration was achieved by random displacement of a single unit to its eight nearest neighboring sites in two dimensions and to its eighteen neighboring sites in three dimensions. The distances between the single unit and the nearest neighboring sites are restricted to a length of 1 and  $\sqrt{2}$ . Each attempted move may change the bond length but the chain connectivity restricts the bond length to 1 and  $\sqrt{2}$ . The excluded volume interaction ensures no more than one bead per lattice site. No bond-crossing is allowed. If one attempted move violates either the

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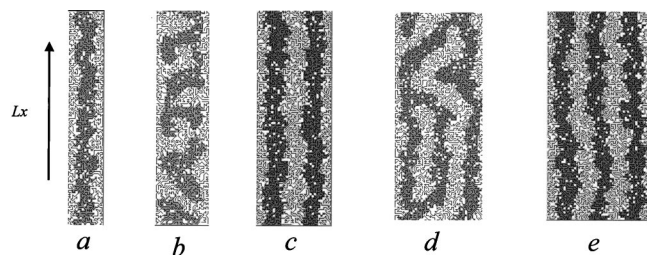


FIG. 1. Morphological patterns for the symmetric diblock copolymers with different gap widths of the parallel-wall boundary in 2D. (a)  $L/N=0.85$ , (b) 1.25, (c) 1.75, (d) 2.15, and (e) 2.5.  $L$ , is proportional to the number of segments of the diblock copolymers, and is the width of the parallel walls.  $N$  is the number of segments of the diblock copolymers;  $Lx/N=5$ .

excluded volume, or no bond-crossing or the bond length restriction, it is rejected. The acceptance or rejection of one attempted move which satisfies both the excluded volume and the bond length conditions is further governed by the

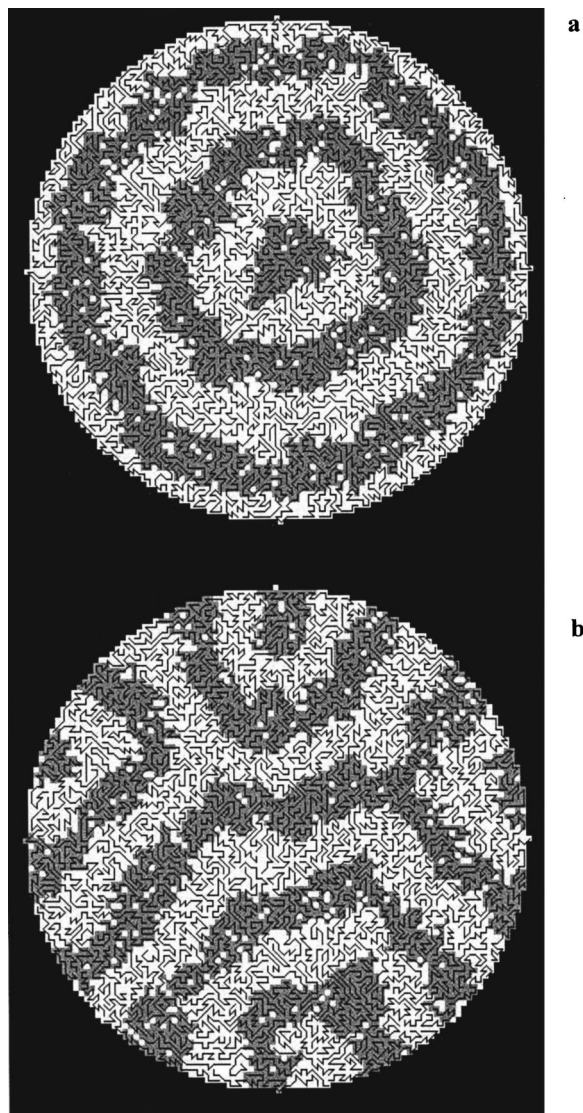


FIG. 2. Morphological patterns for a circle boundary in 2D;  $R/N=2.3$ .  $R$  is the radius of the circle. (a) There are interactions between the boundary and the diblock copolymers and (b) there are no interactions between the boundary and the diblock copolymers.

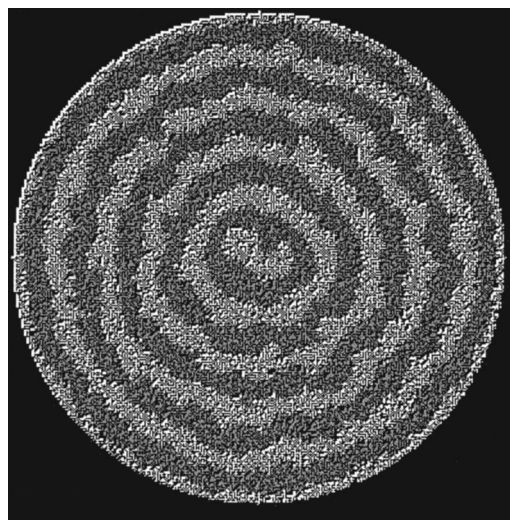


FIG. 3. Morphological patterns for a circle boundary in 2D;  $R/N=4.8$ .

Metropolis Rule,<sup>14</sup> namely, it is accepted if the energy change,  $\Delta E$ , is negative, otherwise, it is accepted with a probability  $P$  as follows:

$$P = \exp(-\Delta E/kT),$$

$\Delta E = (\Delta N_{AA}\epsilon_{AA} + \Delta N_{BB}\epsilon_{BB} + \Delta N_{AB}\epsilon_{AB} + \Delta N_{AC}\epsilon_{AC} + \Delta N_{BC}\epsilon_{BC})$  is the energy change of the movement,  $\Delta N$  is the difference between the number of nearest-neighboring pairs of the sites occupied by monomers or by boundaries before and after movement,  $\epsilon$  is the reduced interaction energy gained after the two neighboring sites are occupied by monomers or boundaries; and the subscripts A, B, and C denote monomers A, B, and boundary units, respectively.

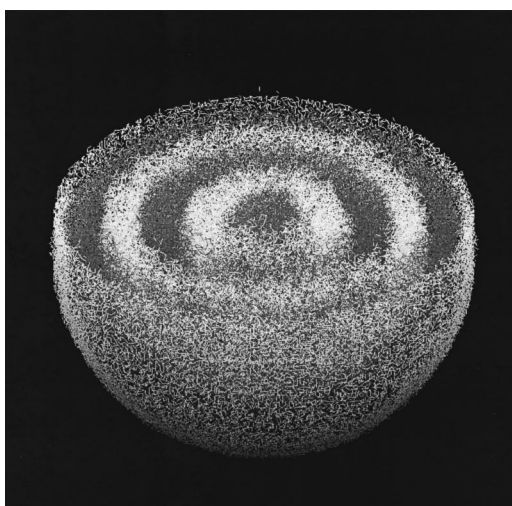
In this simulation, put  $\epsilon_{AB}=1$ ,  $\epsilon_{AA}=\epsilon_{BB}=0$ ,  $\epsilon_{AC}=-1$ ,  $\epsilon_{BC}=1$ , which ensure that the A block is immiscible with the B block, and the boundary attracts the A block and repulses the B block. First, the system was annealed in an athermal state ( $1/kT=0$ ) for a long time to reach equilibrium disorder state. Then the system was quenched to a new state ( $1/kT=0.5$ ). The process of phase separation in this state was simulated.

## RESULTS AND DISCUSSION

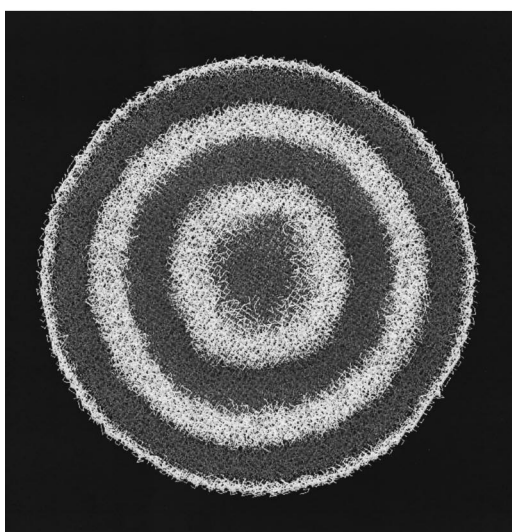
Figure 1 shows the simulation results of self-assemble structures for the symmetric diblock copolymers in the confined state with parallel strip boundary. It can be seen that a strip self-assemble structure was formed. As expected, the boundary intersurface was covered by the segments of the A-block. The number of strips depended on the gap width of the parallel walls. It was also found that there is "disorder state," i.e., the strip phase structure was frustrated, when transiting from one strip to two strips or from two strips to three ones. The investigation on the mechanism of the "disorder state" is currently underway.

The phase structure shown Fig. 2 was related to the circle-shape boundary. The self-assemble structures of circle strips were formed [see Fig. 2(a)]. When there were no interactions between the circle-shape boundary and the diblock copolymers, random phase structure was formed [see Fig.





(a)

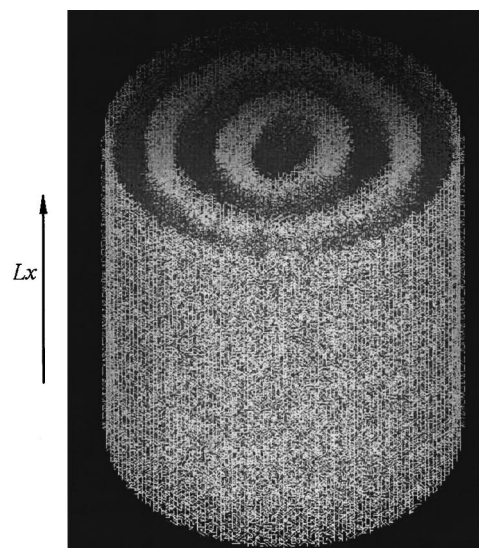


(b)

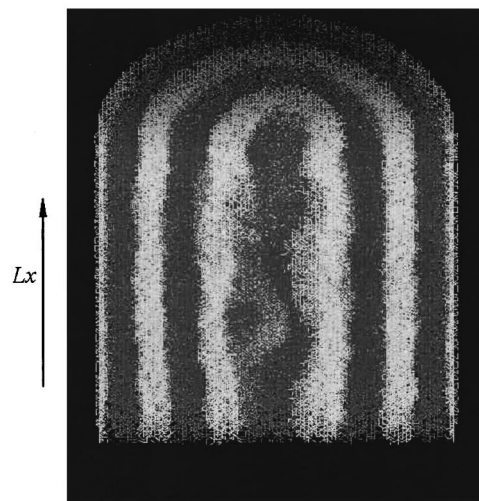
FIG. 4. Morphological patterns for a spherical boundary in 3D;  $R/N=2.3$ .  $R$  is the radius of the sphere. (a) Three dimensions and (b) its section structure.

2(b)]. The arrangement order of A and B blocks of the diblock copolymer in the self-assemble structure shown in Fig. 2(a) was B-AA-BB-AA-BB-A from the center. However the arrangement order depended on the radius of the circle. With changing the radius of the circle, the center could be the A block or B block. An example was given in Fig. 3. The arrangement order of A and B blocks in the self-assemble structure shown in Fig. 3 was A-BB-AA-BB-AA-BB-AA-BB-AA-BB-A.

Figure 4 shows the self-assemble structure for the symmetric diblock copolymer related to the sphere-shape boundary. In the sphere-shape boundary, it can be seen that the diblock copolymers were arranged to form a core-multishell self-assemble structure [see Fig. 4(a)]. The core shown in Fig. 4(a) was the B block. Figure 4(b) shows its section structure, which is similar to that in the circle-shape boundary. In a barrel-shape boundary, the symmetric diblock copolymers were arranged to form a multibarrel-layer self-assemble structure was found [see Figs. 5(a) and 5(b)].



(a)



(b)

FIG. 5. Morphological patterns for a barrel boundary in 3D;  $R/N=2.3$ .  $R$  is the radius of the cylinder. (a) Three dimensions and (b) its section structure;  $Lx/N=5$ .

The above computer simulation results indicate that the novel phase structure can be formed by adjusting the boundary shape and interactions. That different boundary shapes and interactions between boundaries and the diblock copolymers resulted in a different self-assemble structure should provide useful information for designing the novel phase structure for polymer materials.

## CONCLUSIONS

(1) Computer simulation results indicate that symmetric diblock copolymers can form different self-assemble structures in two-dimensional or three-dimensional confined states in which there are interactions between boundaries and the diblock copolymers.

(2) Self-assemble morphology of the diblock copolymers can be controlled by adjusting the boundary shape and inter-

action, which resulted in the formation of novel self-assemble structures, e.g., strip, circle, core-multishell, and multibarrel-layer structures.

## ACKNOWLEDGMENTS

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