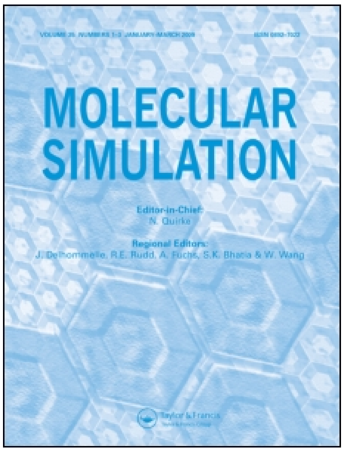

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Depletion phenomenon in diblock copolymer films: a dissipative particle dynamics simulation

Yi Xu[a]; Jian Feng[b]; Zhang Zhang[a]; Yong Wang[a]; Jie Chen[a]; Xian Zhu[a]
[a] Department of Chemical Engineering and Technology, School of Environmental and Chemical Engineering, Shanghai University, Shanghai, P.R. China [b] Department of Chemistry and Life Science, Chuzhou University, Chuzhou, Anhui Province, P.R. China

To cite this Article Xu, Yi , Feng, Jian , Zhang, Zhang , Wang, Yong , Chen, Jie and Zhu, Xian(2010) 'Depletion phenomenon in diblock copolymer films: a dissipative particle dynamics simulation', Molecular Simulation, 36: 6, 468 — 473

To link to this Article: DOI: 10.1080/08927021003664033

URL: http://dx.doi.org/10.1080/08927021003664033

Molecular Simulation
Vol. 36, No. 6, May 2010, 468–473

Depletion phenomenon in diblock copolymer films: a dissipative particle dynamics simulation

Yi Xu[a]*, Jian Feng[b], Zhang Zhang[a], Yong Wang[a], Jie Chen[a] and Xian Zhu[a]

[a]*Department of Chemical Engineering and Technology, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, P.R. China;* [b]*Department of Chemistry and Life Science, Chuzhou University, Chuzhou 239012, Anhui Province, P.R. China*

(*Received 18 September 2009; final version received 30 January 2010*)

A tentative simulation study has been carried out on the depletion phenomenon in diblock copolymer films through dissipative particle dynamics technology. Results indicate that a depletion layer appears in nearly all the systems with strong interaction between different components, accompanied with weak interaction between the component and the boundary. The system temperature plays a dominant role in the thickness of the depletion layer, on which the component fraction also has an effect to a certain extent. The findings can give support to relevant application processes.

Keywords: depletion phenomenon; diblock copolymer films; dissipative particle dynamics

1. Introduction

Block copolymers have received much attention over the past few decades due to their ability to form various ordered mesostructures, whose phase separation occurs only on a microscopic level because the different blocks are chemically linked. The resulting microphases exhibit classical morphologies such as lamellas, rods, spheres, bicontinuous structures [1,2], leading to novel properties and wide applications [3–6]. The microscopic morphology originated from the self-assembly of the block copolymer can be controlled not only by varying the symmetry of the block copolymer but also by introducing external geometrical confinement to the system. While the majority of relevant research has concentrated on bulk systems, more efforts based on theoretical analysis and computer simulation have been made to understand phase-separation behaviours of block copolymers in thin films. As for diblock systems, there have been investigations dealing with the cases of one- [7–17], two- [18–27] and even three- [18,28,29] dimensional confinements, most of which have focused on the apparent process of microstructure formation and transition; however, less attention, even in the simplest case of one-dimensional confinement, has been paid to the statistical information of the microstructure, which can help us gain an insight into diblock copolymer films and make use of these systems better.

Depletion is a famous phenomenon widely existing in polymer–colloid mixtures, at surfaces and interfaces, which has attracted increasing attention [30–38]. For example, employing Langmuir monolayers of highly asymmetric diblock copolymers as a model tethered chain system, Kent et al. [30] examined the structure and free energy of tethered layers over an order of magnitude in both surface density (σ) and molecular weight (M) in theta solvent conditions and observed a depletion layer at the air–liquid interface which increases with M and is independent of σ. Their subsequent work aimed at poor solvent conditions [31] disclosed that the thickness of the depletion layer increases slightly with decreasing temperature. Fleer and co-workers [34] derived a simple, analytical, general continuum expression for the depletion thickness near a flat wall in the mean-field approximation, which is easily extended to spherical geometry. As a relevant study, they [35] recently suggested to use a linear combination of two limits (dilute and semidilute) to obtain an extremely simple equation that can describe the concentration dependence of the osmotic pressure and the depletion thickness over the entire range of concentrations. By means of density functional theory, Chen et al. [37] investigated the recognition of homopolymer at nano-patterned surface, in which the transition from depletion at low packing fractions to adsorption and double-layer adsorption at high packing fractions was satisfactorily described. Recurring to the real-space version of self-consistent field theory, Wang and co-workers [38] theoretically investigated the phase separation of asymmetric diblock copolymer near the surfaces in selective solvents, whose results showed that the depletion layer near the surface contributes much to the micelle formation of the block copolymer, and the self-assembled morphologies stay near the walls with the distance of the order of the radius of gyration of the block copolymer.

Is it possible for the depletion phenomenon to exist in block copolymer films? As a tentative work, density profiles in diblock copolymers with one-dimensional

---

*Corresponding author. Email: tree2000xy@shu.edu.cn

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927021003664033
http://www.informaworld.com

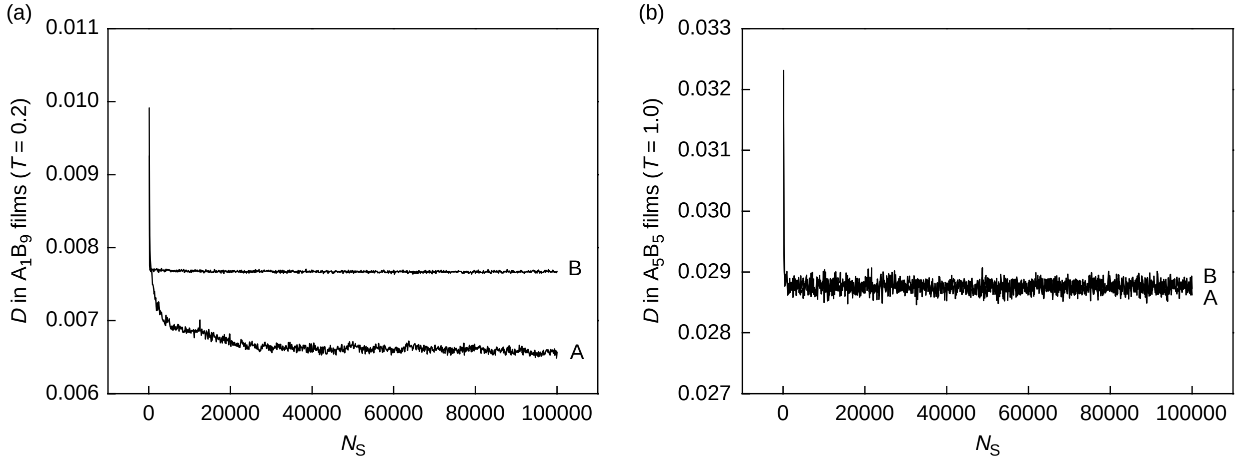

Figure 1. Evolution of the diffusion coefficient of DPD particles with the simulation time increasing in (a) A_1B_9 ($T = 0.2$) and (b) A_5B_5 ($T = 1.0$) films, separately.

confinement, especially their dependence on the system temperature, have been explored by means of the dissipative particle dynamics (DPD) method, which has played an important role in tracing the complex dynamic processes in the formation of polymer microphases.

2. Simulation method and model construction

The DPD method was first introduced by Hoogerbrugge and Koelman [39,40] and gradually improved by various authors [41,42]. It has been applied covering a wide field and proved to be a versatile simulation technique for complex fluids on the mesoscopic scale [43–45]. The elementary units in DPD are fluid elements or coarse-grained soft particles representing a small region of fluid that contains a group of molecules. The time evolution is governed by Newtonian equations of motion [42]. The interparticle interacting force f_i contains three parts, each of them is pairwise additive,

$$f_i = \sum_{j \neq i} (F_{ij}^{\mathrm{C}} + F_{ij}^{\mathrm{D}} + F_{ij}^{\mathrm{R}}), \tag{1}$$

where the conservative force F_{ij}^{C} is a soft repulsive force acting along the line of centres, the dissipative force F_{ij}^{D} and the random force F_{ij}^{R} act as heat sink and source, respectively, to provide a thermostat for the whole system.

The diblock copolymer in simulations is modelled as a linear free chain consisting of 10 DPD soft particles with the same diameter r_{c}, which are connecting one by one through additional harmonic spring force $F_{ij}^{\mathrm{S}} = Cr_{ij}$. The initial linking bond lengths between the neighbouring particles are all set equal to a unit length. In this work, we adopted a three-dimensional rectangle simulation cell of size $30(x) \times 30(y) \times 5(z)$ with periodic boundary conditions applied in the x, y directions. As a confinement, two impenetrable boundaries are set in the z-direction, both of which give each particle an identical repulsion $a_{\mathrm{pb}} = 25$ for keeping it away from either boundary. In order to prevent any particle from moving beyond the system, particles running into the z-direction boundaries can be bounced into a symmetric trace, i.e. the velocity direction of each bounced particle is not changed in the x and y directions, while it is absolutely opposite to that before being bounced in the z-direction. The interaction energy between particles of different types $a_{ij} = 50$, while, for the same type, $a_{ii} = 25$. The number density ρ equals to 3.0 and the total number of copolymers in the system is 1350. The reduced temperature of the whole system $k_{\mathrm{B}}T$ (denoted as T in the next sections for simplicity) is set in the range of $[0.2, 1.0]$ with fixed interval. The standard deviation of random force σ is equal to 3.67 and the spring parameter C is equal to 4.0. The standard velocity-Verlet scheme [42] is adopted for integration and the integral step $\Delta t = 0.05$. For each system, 100,000 time steps per simulation are carried out.

3. Simulation results and discussion

The diffusivity of a DPD particle is a specific parameter which characterises the DPD fluid and can be regarded as the ratio between the time for fluid particles to diffuse a certain distance and the time for hydrodynamic interactions to reach a steady state on the same distance [42]. Hence, the diffusion coefficient of each particle in a single DPD simulation can be employed to examine the system equilibrium [46–48]. It can be derived by calculating the mean square displacement of each type of bead according

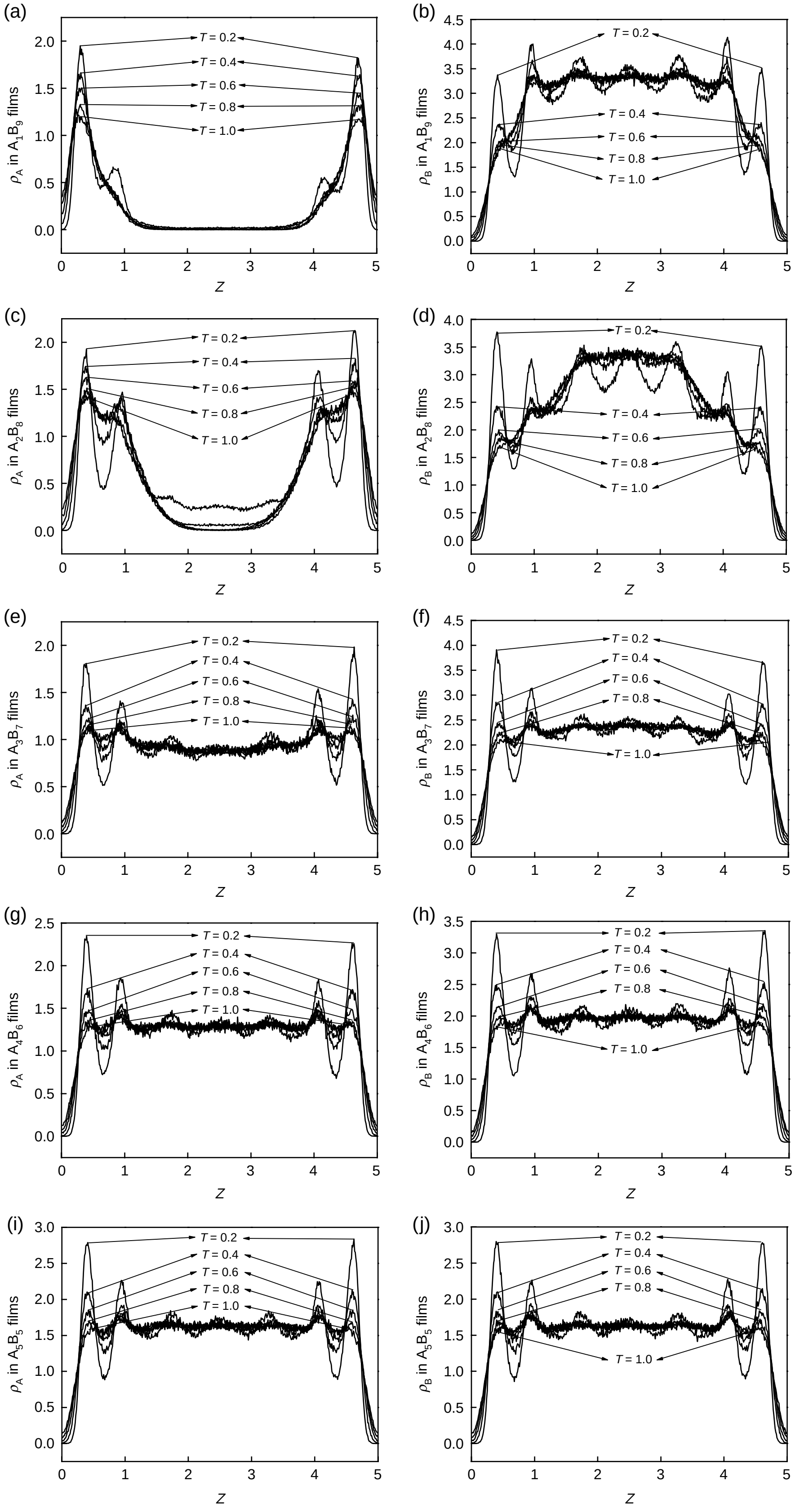

Figure 2. Temperature dependence of density profiles in the *z*-direction in AB diblock copolymer films. (a,b) A_1B_9 films, (c,d) A_2B_8 films, (e,f) A_3B_7 films, (g,h) A_4B_6 films and (i,j) A_5B_5 films.

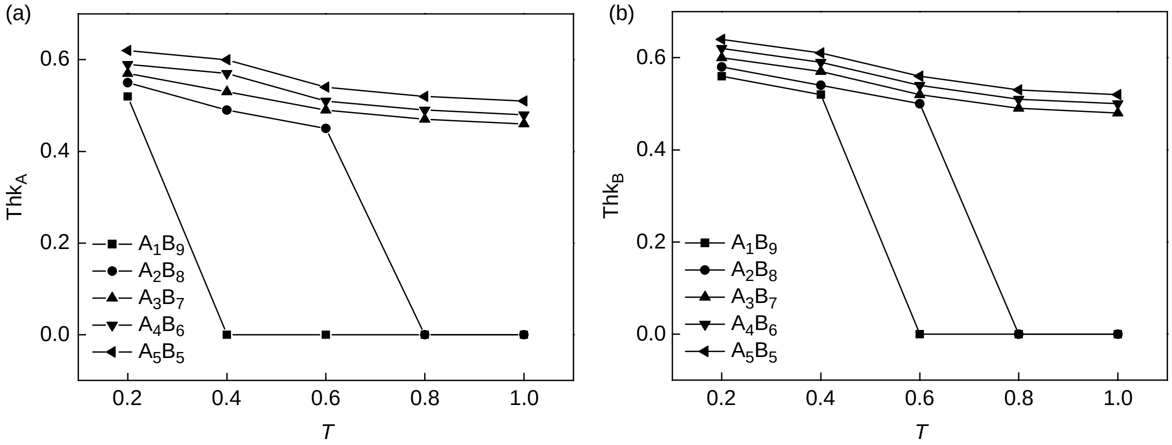

Figure 3. Temperature dependence of the thickness of (a) A and (b) B depletion layers in AB diblock copolymer films.

to the Einstein equation [49]

$$D = \lim_{t\to\infty} \frac{1}{6Nt} \left\langle \sum_{i=1}^{N} [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \right\rangle, \qquad (2)$$

where N is the number of particles in the simulation system, t denotes the simulation evolving time, $\mathbf{r}_i(0)$ and $\mathbf{r}_i(t)$ represent the position vector of particle i at time 0 and t, respectively.

Figure 1 shows the evolution of the diffusion coefficient of DPD particles (D) with the simulation time steps (N_S) in representative A_1B_9 ($T = 0.2$) and A_5B_5 ($T = 1.0$) films. In the latter case, the simulated diffusion coefficients of A and B particles are too close to be distinct from each other. It is obvious that there are nearly no big changes but small fluctuations in the diffusion coefficient of either DPD particle after the simulation is carried out for a short time (up to 20,000 time steps), which indicates that the system has already achieved equilibrium. According to the time evolution of diffusion coefficients, it is reasonable that 100,000 time steps per simulation are indeed sufficient for simulation equilibrium.

3.1 General characteristic of density profiles

Figure 2 shows how density profiles of A and B components, ρ_A and ρ_B, in the confinement-introduced z-direction depend on the system temperature T in AB diblock copolymer films. Apparently, the densities nearest to both sides in the z-direction are relatively higher, i.e. both A and B components prefer assembling closest to the impenetrable boundaries, for the repulsion between the component and the boundary is weaker than that between different components. In addition, a higher temperature can induce inside components to move more actively and consequently distribute over a larger range in diblock copolymer films, which is embodied distinctly in gradually lower peaks nearest to the boundaries. At the same temperature, the more the composition fraction is, the higher the density everywhere in the film is.

3.2 Depletion layer

A distinct characteristic in Figure 2(a)–(j) is that a negative peak lies in the vicinity of the positive peak closest to either side, which indicates a sudden density drop. The mechanism for the appearance of this phenomenon deserves more attention. As mentioned previously, compared to the interaction between different components, the interaction between the component and the boundary is much weaker leading to more A and B components gathering nearest to both boundaries. As a consequence, a local effect occurs in which a layer with relatively higher component density appears closest to either side, in the vicinity of which a layer with relatively lower component density arises, i.e. the depletion layer. Unlike other fluctuations in the density profile, the peak value of the negative peak representing the depletion layer is much smaller, indicating much lower inside component density. Thus, a piece of useful information can be obtained therefrom that the density distribution of either component in diblock copolymer films can be controlled and adjusted effectively through its interaction with other components and boundaries.

The influence of the system temperature on the density profiles can be reflected as well in the thickness of the depletion layer in diblock copolymer films. Figure 3 shows the temperature dependence of the thickness of the A(Thk_A) and B(Thk_B) depletion layer in AB diblock copolymer films, in which each value is obtained by averaging the thicknesses of two depletion peaks in the same system. Obviously, the system temperature has a significant influence on the depletion layer – a higher temperature can make the depletion layer thinner, i.e. Thk descends gradually as T ascends, and even absent in some cases, i.e. Thk equals to zero in A_1B_9 and A_2B_8 films, which can be ascribed chiefly to the aforementioned weakening effect of high temperature on the assemble behaviour of A and B components nearest to both sides inducing the tendency to inside hypodispersion in the z-direction. On the composition dependence, when the fraction of component A (f_A) is not comparable to that of component B (f_B), the number of possible A–B repulsive pairs in the film is relatively less. Consequently, the gathering effect of components closest to both sides is not so distinct, and even too weak to form a depletion layer in some cases. As f_A rises gradually to 0.5, i.e. approaches f_B, the possibility of A–B repulsion increases evidently, leading to more and more A and B components running towards both sides for less repulsion. The more intensive the assembling behaviour of components nearest to both sides is, the thicker the relevant depletion layer is.

4. Conclusions

A preliminary investigation has been made on the depletion phenomenon in diblock copolymer films by means of DPD simulations. Results show that the depletion layer can form in almost all the systems with strong interaction between different components, together with weak interaction between the component and the boundary. Both the system temperature and the component fraction have an influence on the thickness of the depletion layer, of which the former is dominant. These findings can provide some guidance for relevant application processes.

Acknowledgements

This work is supported by the Shanghai Leading Academic Discipline Project (No. S30109), the R&D Special Fund of Excellent Young Teachers of Universities in Shanghai, the Developmental Fund of Scientific Technology of Shanghai University and the Innovation Fund of Shanghai University.

References

[1] F.S. Bates and G.H. Frederickson, *Block copolymer thermodynamics – Theory and experiment*, Annu. Rev. Phys. Chem. 41 (1990), pp. 525–557.

[2] F. Corberi, G. Gonnella, and A. Lamura, *Two-scale competition in phase separation with shear*, Phys. Rev. Lett. 83 (1999), pp. 4057–4060.

[3] W.A. Lopes and H.M. Jaeger, *Hierarchical self-assembly of metal nanostructures on diblock copolymer scaffolds*, Nature (Lond.) 414 (2001), pp. 735–738.

[4] M. Templin, A. Franck, A. DuChesne, H. Leist, Y.M. Zhang, R. Ulrich, V. Schadler, and U. Wiesner, *Organically modified aluminosilicate mesostructures from block copolymer phases*, Science 278 (1997), pp. 1795–1798.

[5] T. Turn-Albrecht, J. Schotter, G.A. Kaestle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C.T. Black, M.T. Tuominen, and T.P. Russell, *Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates*, Science 290 (2000), pp. 2126–2129.

[6] M. Park, C. Harrison, P.M. Chaikin, R.A. Register, and D.H. Adamson, *Block copolymer lithography: Periodic arrays of ~10 to the 11th power holes in 1 square centimeter*, Science 276 (1997), pp. 1401–1404.

[7] M.S. Turner, *Equilibrium properties of a diblock copolymer lamellar phase confined between flat plates*, Phys. Rev. Lett. 69 (1992), pp. 1788–1791.

[8] D.G. Walton, G.J. Kellogg, A.M. Mayes, P. Lambooy, and T.P. Russell, *A free energy model for confined diblock copolymers*, Macromolecules 27 (1994), pp. 6225–6228.

[9] H.J. Angerman, A. Johner, and A.N. Semenov, *Microphase separation in thin block copolymer films: A weak segregation mean-field approach*, Macromolecules 39 (2006), pp. 6210–6220.

[10] M.J. Fasolka, P. Banerjee, A.M. Mayes, G. Pickett, and A.C. Balazs, *Morphology of ultrathin supported diblock copolymer films: Theory and experiment*, Macromolecules 33 (2000), pp. 5702–5712.

[11] G.T. Pickett and A.C. Balazs, *Equilibrium orientation of confined diblock copolymer films*, Macromolecules 30 (1997), pp. 3097–3103.

[12] M.W. Matsen, *Thin films of block copolymer*, J. Chem. Phys. 106 (1997), pp. 7781–7791.

[13] W.H. Tang and T.A. Witten, *Quenched degrees of freedom in symmetric diblock copolymer thin films*, Macromolecules 31 (1998), pp. 3130–3135.

[14] T. Geisinger, M. Muller, and K. Binder, *Symmetric diblock copolymers in thin films. I. Phase stability in self-consistent field calculations and Monte Carlo simulations*, J. Chem. Phys. 111 (1999), pp. 5241–5250.

[15] T. Geisinger, M. Muller, and K. Binder, *Symmetric diblock copolymers in thin films. II. Comparison of profiles between self-consistent field calculations and Monte Carlo simulations*, J. Chem. Phys. 111 (1999), pp. 5251–5258.

[16] J. Feng, H. Liu, and Y. Hu, *Microdomain morphology of symmetrical diblock copolymer thin films confined in a slit*, Macromol. Theor. Simul. 11 (2002), pp. 549–555.

[17] J. Feng, H. Liu, and Y. Hu, *Asymmetric diblock copolymer thin film confined in a slit: Microphase separation and morphology*, Macromol. Theor. Simul. 11 (2002), pp. 556–565.

[18] X. He, M. Song, H. Liang, and C. Pan, *Self-assembly of the symmetric diblock copolymer in a confined state: Monte Carlo simulation*, J. Chem. Phys. 114 (2001), pp. 10510–10513.

[19] G.J.A. Sevink, A.V. Zvelindovsky, J.G.E.M. Fraaije, and H.P. Huinink, *Morphology of symmetric block copolymer in a cylindrical pore*, J. Chem. Phys. 115 (2001), pp. 8226–8230.

[20] P. Chen, X. He, and H. Liang, *Effect of surface field on the morphology of a symmetric diblock copolymer under cylindrical confinement*, J. Chem. Phys. 124 (2006), 104906.

[21] B. Yu, P. Sun, T. Chen, Q. Jin, D. Ding, B. Li, and A.C. Shi, *Confinement-induced novel morphologies of block copolymers*, Phys. Rev. Lett. 96 (2006), 138306.

[22] W.H. Li, R.A. Wickham, and R.A. Garbary, *Phase diagram for a diblock copolymer melt under cylindrical confinement*, Macromolecules 39 (2006), pp. 806–811.

[23] J. Feng and E. Ruckenstein, *Morphologies of AB diblock copolymer melts confined in nanocylindrical tubes*, Macromolecules 39 (2006), pp. 4899–4906.

[24] J. Feng and E. Ruckenstein, *Morphology transitions of AB diblock copolymer melts confined in nanocylindrical tubes*, J. Chem. Phys. 125 (2006), 164911.

[25] J. Feng, H. Liu, and Y. Hu, *Mesophase separation of diblock copolymer confined in a cylindrical tube studied by dissipative particle dynamics*, Macromol. Theor. Simul. 15 (2006), pp. 674–685.

[26] X. Xiao, Y. Huang, H. Liu, and Y. Hu, *Morphology transition of block copolymers under curved confinement*, Macromol. Theor. Simul. 16 (2007), pp. 732–741.

[27] M. Heckmann and B. Drossel, *Cylindrical phase of block copolymers in thin films*, Macromolecules 41 (2008), pp. 7679–7686.

[28] J.G.E.M. Fraaije and G.J.A. Sevink, *Model for pattern formation in polymer surfactant nanodroplets*, Macromolecules 36 (2003), pp. 7891–7893.

[29] J. Feng, H. Liu, and Y. Hu, *Micro-phase separation of diblock copolymer in a nanosphere: Dissipative particle dynamics approach*, Fluid Phase Equilibr. 261 (2007), pp. 50–57.

[30] M.S. Kent, J. Majewski, G.S. Smith, L.T. Lee, and S. Satija, *Tethered chains in theta solvent conditions: An experimental study involving Langmuir diblock copolymer monolayers*, J. Chem. Phys. 108 (1998), pp. 5635–5645.

[31] M.S. Kent, J. Majewski, G.S. Smith, L.T. Lee, and S. Satija, *Tethered chains in poor solvent conditions: An experimental study involving Langmuir diblock copolymer monolayers*, J. Chem. Phys. 110 (1999), pp. 3553–3565.

[32] J. van der Gucht, N.A.M. Besseling, and G.J. Fleer, *Chain-length dependence of the polymer surface excess near the adsorption/depletion transition*, Macromolecules 35 (2002), pp. 2810–2816.

[33] D. Zhou, N. Xu, L. Li, G. Ji, and G. Xue, *Surface reactions on polymer thin films studied by surface-enhanced Raman scattering*, J. Phys. Chem. B 107 (2003), pp. 2748–2751.

[34] G.J. Fleer, A.M. Skvortsov, and R. Tuinier, *Mean-field equation for the depletion thickness*, Macromolecules 36 (2003), pp. 7857–7872.

[35] G.J. Fleer, A.M. Skvortsov, and R. Tuinier, *A simple relation for the concentration dependence of osmotic pressure and depletion thickness in polymer solutions*, Macromol. Theor. Simul. 16 (2007), pp. 531–540.

[36] E. Reister and M. Muller, *Formation of enrichment layers in thin polymer films: The influence of single chain dynamics*, J. Chem. Phys. 118 (2003), pp. 8476–8488.

[37] H. Chen, Z. Ye, C. Peng, H. Liu, and Y. Hu, *Density functional theory for the recognition of polymer at nanopatterned surface*, J. Chem. Phys. 125 (2006), 204708.

[38] R. Wang, Y.L. Chen, J. Hu, and G. Xue, *Depletion-induced surface alignment of asymmetric diblock copolymer in selective solvents*, J. Chem. Phys. 129 (2008), 044907.

[39] P.J. Hoogerbrugge and J.M.V.A. Koelman, *Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics*, Europhys. Lett. 19 (1992), pp. 155–160.

[40] J.M.V.A. Koelman and P.J. Hoogerbrugge, *Dynamic simulations of hard-sphere suspensions under steady shear*, Europhys. Lett. 21 (1993), pp. 363–368.

[41] P. Español and P.B. Warren, *Statistical mechanics of dissipative particle dynamics*, Europhys. Lett. 30 (1995), pp. 191–196.

[42] R.D. Groot and P.B. Warren, *Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation*, J. Chem. Phys. 107 (1997), pp. 4423–4435.

[43] R.D. Groot and T.J. Madden, *Dynamic simulation of diblock copolymer microphase separation*, J. Chem. Phys. 108 (1998), pp. 8713–8724.

[44] R.D. Groot, T.J. Madden, and D.J. Tildesley, *On the role of hydrodynamic interactions in block copolymer microphase separation*, J. Chem. Phys. 110 (1999), pp. 9739–9749.

[45] S. Yuan, Z. Cai, and G. Xu, *Mesoscopic simulation of aggregates in surfactant/oil/water systems*, Chinese J. Chem. 21 (2003), pp. 112–116.

[46] X. Cao, G. Xu, Y. Li, and Z. Zhang, *Aggregation of poly(ethylene oxide)–poly(propylene oxide) block copolymers in aqueous solution: DPD simulation study*, J. Phys. Chem. A 109 (2005), pp. 10418–10423.

[47] C. Yang, X. Chen, H. Qiu, W. Zhuang, Y. Chai, and J. Hao, *Dissipative particle dynamics simulation of phase behavior of aerosol OT/water system*, J. Phys. Chem. B 110 (2006), pp. 21735–21740.

[48] S. Chen, C. Guo, G. Hu, H. Liu, X. Liang, J. Wang, J. Ma, and L. Zheng, *Dissipative particle dynamics simulation of gold nanoparticles stabilization by PEO–PPO–PEO block copolymer micelles*, Colloid Polym. Sci. 285 (2007), pp. 1543–1552.

[49] H. Wu, J. Xu, X. He, Y. Zhao, and H. Wen, *Mesoscopic simulation of self-assembly in surfactant oligomers by dissipative particle dynamics*, Colloids Surf. A 290 (2006), pp. 239–246.