Dynamic Density Functional Simulations for Morphological Transition Dynamics of Block Copolymer Micelles

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Amphiphilic block copolymers form micellar structures in selective solvents. It is known that micellar structures are controlled by several factors such as the block copolymer architecture or the solvent quality [1]. In this work we study morphological transition dynamics in amphiphilic diblock copolymer solutions by using the dynamic density functional model [2].

In the dynamic density functional model, a state of the system is described by density fields for hydrophilic subchains (A), hydrophobic subchains (B), and solvents (S). The time evolution of the density fields $\rho_i(\boldsymbol{r}.t)(i = A, B, S)$ is described by the following dynamic equation.

$$\frac{\partial \rho_i(\boldsymbol{r},t)}{\partial t} = \nabla \cdot \left[\frac{\rho_i(\boldsymbol{r},t)}{\zeta} \nabla \frac{\delta \mathcal{F}\left[\{\rho_i\}\right]}{\delta \rho_i(\boldsymbol{r},t)} \right] + \nabla \cdot \left[\sqrt{2\tilde{\beta}^{-1} k_B T/\zeta} \sqrt{\rho_i(\boldsymbol{r})} \boldsymbol{w}_i(\boldsymbol{r},t) \right] \tag{1}$$

where ζ is the friction coefficient, $\mathcal{F}\left[\{\rho_i\}\right]$ is the free energy functional, k_B is the Boltzmann constant, T is the temperature, and $\tilde{\beta}^{-1}$ is the noise strength parameter. $\boldsymbol{w}_i(\boldsymbol{r},t)$ is the Gaussian white noise which satisfies $\langle \boldsymbol{w}_i(\boldsymbol{r},t) \rangle = 0$ and $\langle \boldsymbol{w}_i(\boldsymbol{r},t) \boldsymbol{w}_j(\boldsymbol{r}',t') \rangle = \delta_{ij} \delta(\boldsymbol{r}-\boldsymbol{r}') \delta(t-t') \mathbf{1}$.

We performed several simulations with various values of the interaction parameter between the hydrophobic subchains and the solvents (χ_{BS}). We started simulations from the results of structural formation dynamics and changed χ_{BS}. Some snapshots of simulations are shown in Fig. 1. We can observe that morphological transitions occur only by changing χ_{BS}.

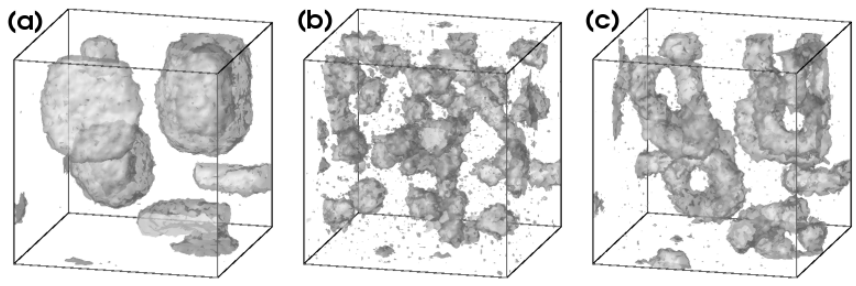

FIG. 1: Snapshots of morphological transition dynamics simulations. Grey surfaces show isodensity surfaces of $\rho_B(\boldsymbol{r}) = 0.5$. (a) initial state ($t = 0$, vesicles and bilayers) and snapshots at $t = 6250$ (in dimensionless unit), (b) $\chi_{BS} = 2.5$ (spheres) and (c) $\chi_{BS} = 3$ (cylinders).

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[2] T. Uneyama, J. Chem. Phys. **126**, 114902 (2007).