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Effect of particle surface selectivity on composite nanostructures in nanoparticle/diblock copolymer mixture dilute solution

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In this study the phase behavior of nanoparticle/diblock copolymer composites in dilute solution has been investigated by the hybrid particle-field (HPF) method. We focus on the influence of particle surface selectivity (i.e. hydrophobic and hydrophilic) on the distribution of nanoparticles in the micelles formed by the diblock copolymers. These two types of particle surface selectivity are simulated systematically. The different competition between the energy from enthalpy and the energy from entropy has been observed in the two kinds of composite systems. Our simulation results show that the particle surface selectivity is a crucial factor for determining the thermodynamic properties in the complex dilute solution, and the morphologies of micelles are controlled by the volume fraction of the nanoparticles. The change of particle distribution in various micelles enriches the composite microstructures that can be formed by nanoparticle and diblock copolymer.

1. Introduction

Nanoparticle/diblock copolymer composites provide a natural approach to produce various ordered structures for the potential applications in functional materials and devices. A big challenge in the field is how to control the distribution of nanoparticles in the complex fluid media. Great progress has been achieved experimentally on the control of spherical nanoparticle location in diblock copolymer melt in the recent decade. The spherical particles were selectively confined in one block domain and assembled into many complex microstructures such as nanowires and nanorings [1–3]. In order to understand the physical essence of these complex microstructures, a variety of theory and simulation methods have been used to investigate the nanoparticle/block copolymer composites [4–12]. For example, Sides et al. developed a hybrid particle-field (HPF) method based on self consistent field theory to investigate the equilibrium structures and properties of polymeric fluids with embedded colloids or nanoparticles [4]. The HPF method is convenient for analyzing complex polymer morphologies with the flexibility of a particle-based simulation that can include particles with a variety of shapes [9], interactions, and surface treatments in a straightforward way.

The investigation of nanoparticle/diblock copolymer composites in dilute solution should be more interesting and complicated, thus it will provide more opportunities for the applications of the composite microstructures in the fields of drug delivery and release, cosmetic industry, food products, and so on [13–18]. It is well known that the amphiphilic diblock copolymers can assemble into various complex micelles in dilute solution [19–22]. The added nanoparticles with different surface selectivity may result in more complicated microstructures. A large number of experimental and theoretical researches have been conducted on the system of nanoparticle/copolymer mixture in solution [23–29]. In order to control the distribution of nanoparticles in the polymeric micelles, experimental researchers have designed many methods to change the surface selectivity of nanoparticles, such as grafting different polymers via a two phase method [26,30,31], coating a phosphatidylthio-ethanol lipid [28] and changing the surface charge [29]. The location of nanoparticles in aggregations formed by block copolymer in solution will critically affects their chemical and physical properties [24]. Theoretical studies have also been utilized to understand the self-assembly behavior of amphiphilic nanoparticle/diblock copolymer mixture in dilute solution. Zhang et al. applied the approach combining self-consistent-field theory (SCFT) and density functional theory (DFT) (SCFT/DFT) to investigate the self-assembly behavior of amphiphilic nanoparticle/diblock copolymer mixture in dilute solution; their results show that the morphologies of block copolymer aggregates and the distribution of particles depends on the concentrations of particles, the size and the selectivity of particles [24]. The complex microstructures of bidisperse nanoparticle/diblock copolymer mixture in dilute solutions have been investigated by the same theoretical approach [32]. Comparing with the SCFT/DFT theory, HPF method

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developed by Sides explicitly contains the particle coordinates as degrees of freedom. Thus it is still necessary to give a comprehensive study concerning the effect of surface selectivity of particles on the various microstructures formed by amphiphilic block copolymers in dilute solution. With this understanding, we try to investigate this issue by the above-mentioned HPF method.

Self-consistent-field theory (SCFT) has been successfully used to explore morphologies assembled by complex architecture copolymers in bulk [33,34]. Liang et al. first extended this method to investigate the aggregation behavior of amphiphilic diblock copolymers in dilute solution [35]. In this article, we extend SCFT dilute solution model to contain the nanoparticles by the HPF method. In the complex system containing amphiphilic diblock copolymers, solvents and nanoparticles, we fix some interactions among components and focus on the surface selectivity of nanoparticles, which is highly concerned by many experimentalists [23,29]. The main purpose is to reveal the underlying physical mechanisms of controlling particle distribution in complex microstructures, which may help to explore the unknown territory in experiment and provide more suitable candidates for designing novel materials.

2. Theoretical model

Real-space self-consistent field theory has been utilized to explore the complex microstructures in much complex solution system [35–38]. Different topology architecture copolymer chains can be considered in a set of effective chemical potential fields, which replace the actual interactions between different components. These chemical potential fields are conjugated to the segment density fields of block species. Solvent molecules are also considered to be in an effective chemical potential field, which have been introduced in the multicomponent homopolymer–solvent mixture system in the earlier work by Hong and Noolandi [39]. By the above field theory model a lots of microstructures such as rod-like micelles, circle-like micelles and vesicles can be observed and analyzed. However, in order to be closer to the practical applications the nanoparticles or collides must be contained. A recent numerical approach i.e. HPF method can help to solve the technical problem. Particles are described by the “cavity” functions, which can be used to implement confinement or particles in numerical SCFT algorithm [40–42]. For a set of m particle positions $r = \{r_1, \ldots, r_m\}$, the local density φ_p of particles is defined by the following function:

$$\varphi_p(r) = \sum_{j=1}^{m} h(|r - r_j|) \tag{1}$$

where $h(r) = \left[1 + \tanh\left(\frac{R_p+\varepsilon-r}{\varepsilon}\right) \cdot \tanh\left(\frac{R_p+\varepsilon+r}{\varepsilon}\right)\right]\Big/2$, R_p is the particle radius, r_j is the particle central position and ε is the interfacial width.

Then we give the free energy of a four component mixture of amphiphilic diblock copolymers with hydrophobic segments (A), hydrophilic segments (B), solvent molecules (S) and spherical particles (P) are involved in volume V:

$$\begin{aligned} F = & -f_C \ln(Q_C/f_C V) - N f_S \ln(Q_S/f_S V) - 1/V \\ & \times \int dr[w_A\phi_A + w_B\phi_B + w_S\phi_S + \xi(\vec{r})(1 - \varphi_P - \phi_A - \phi_B - \phi_S)] + 1/V \\ & \times \int dr[\chi_{AB}N\phi_A\phi_B + \chi_{AS}N\phi_A\phi_S + \chi_{BS}N\phi_B\phi_S + \chi_{AP}N\phi_A\varphi_P \\ & + \chi_{BP}N\phi_B\varphi_P + \chi_{SP}N\phi_S\varphi_P] \end{aligned} \tag{2}$$

where N is the length of the diblock copolymer chain. The length fractions of the AB block copolymers are l_A, and $l_B = 1 - l_A$. The volume fractions of the AB diblock copolymers, solvents and particles in the dilute solution are f_C, f_S and f_P. χ_{ij} is the Flory-Huggins interaction parameter between components i and j, and ϕ_A, ϕ_B, ϕ_S, and φ_P are the densities of the blocks A, B, the solvent S and the particle P, respectively. $\xi(\vec{r})$ is the pressure field which ensures the incompressibility, $Q_C = \int d\vec{r} q(\vec{r}, 1)$ is the partition function of a single copolymer chain and $Q_S = \int d\vec{r} \exp[-w_S(\vec{r})/N]$ is the partition function of the solvent. The end-segment distribution function $q(\vec{r}, s)$ gives the probability of finding segment s at position $\vec{r}$, which satisfies the following modified diffusion equation:

$$\frac{\partial q(\vec{r}, s)}{\partial s} = \nabla^2 q(\vec{r}, s) - \omega(\vec{r}, s) q(\vec{r}, s) \tag{3}$$

The initial condition of this equation is $q(\vec{r}, 0) = 1$. ω is ω_A when $0 < s < l_A$ and ω is ω_B when $1 - l_A < s < 1$. The two ends of the polymer chains are distinct, so a second end-segment distribution function $q^+(\vec{r}, s)$ is needed, which also satisfies Eq. (3). In this case ω is ω_B when $0 < s < l_B$ and ω is ω_A when $1 - l_B < s < 1$. For the solution of the diffusion Eq. (3), we employ the pseudo-spectral method proposed by Rasmussen et al. [43,44], which has higher stability and accuracy than the spatial discretization. A fast Fourier transformation (FFTW) package has been used to ensure the precision of the solution [45].

The self-consistency equations are obtained by differentiating Eq. (2) with respect to the density field, the chemical potential fields and the pressure field:

$$w_A = \chi_{AB}N(\phi_B - f_B) + \chi_{AS}N(\phi_S - f_S) + \chi_{AP}N(\varphi_P - f_P) + \xi \tag{4}$$

$$w_B = \chi_{AB}N(\phi_A - f_A) + \chi_{BS}N(\phi_S - f_S) + \chi_{BP}N(\varphi_P - f_P) + \xi \tag{5}$$

$$w_S = \chi_{AS}N(\phi_A - f_A) + \chi_{BS}N(\phi_B - f_B) + \chi_{SP}N(\varphi_P - f_P) + \xi \tag{6}$$

$$\phi_A(\vec{r}) = \frac{f_C V}{Q_C} \int_0^{l_A} ds q(\vec{r}, s) q^+(\vec{r}, 1 - s) \tag{7}$$

$$\phi_B(\vec{r}) = \frac{f_C V}{Q_C} \int_{l_A}^{1} ds q(\vec{r}, s) q^+(\vec{r}, 1 - s) \tag{8}$$

$$\phi_S(\vec{r}) = \frac{f_S V}{Q_s} \exp(-w_s(\vec{r})/N) \tag{9}$$

$$\phi_A + \phi_B + \phi_S = 1 - \varphi_P \tag{10}$$

The force acting on particle j can be calculated by the following convolution integral:

$$\vec{F}_j = -\frac{\partial F}{\partial r_j} = -\int d\vec{r} [\chi_{AP}\phi_A(\vec{r}) + \chi_{BP}\phi_B(\vec{r}) + \chi_{SP}\phi_S + \xi(\vec{r})] \cdot \frac{1}{r} \frac{dh(r - r_j)}{dr_j} \vec{r} \tag{11}$$

Then we can update the particle positions according to a Brownian dynamic (BD) algorithm:

$$\Delta\vec{r}_j = \beta D \Delta t \vec{F}_j + \vec{R}_j \tag{12}$$

where $\beta D \Delta t$ is the displacement coefficient and $\vec{R}_j$ is a Gaussian random variable. The iteration process of searching the equilibrium structures is consistent with the HPF method [4].The algorithm outline is: (i) Solve the mean field SCFT equations and find the new density and potential fields; (ii) Calculate the $\vec{F}_j$ by an FFT-inverse FFT pair; (iii) Update the particle positions and avoid the particle overlaps; (iv) Return to the step (i). The iteration repeats until the morphology is stable.

The calculations are carried out in two-dimensional space with a 220 × 220 square lattice with periodic boundary. The side length is $L_x = L_y = 36.67R_g$ (R_g is the radius of gyration of the diblock copolymer). The volume fraction of the diblock copolymer is set as $f_c = 0.1$, which can ensure the system is a dilute solution. The