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Morphology transformation of a vesicle induced by a pair of encapsulated particles

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HIGHLIGHTS

- We study the morphology transformation of a vesicle induced by two nano-particles.
- We predict different vesicle structures for various distances of two particles.
- The results are of interest to the interactions of vesicles and particles.

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ABSTRACT

We begin with a pair of spherical particles encapsulated in a vesicle and solve the problem within the self-consistent field theory (SCFT) to investigate the morphology transformation of the vesicle induced by two nano-particles. The vesicles are based on amphiphilic diblock copolymer AB in homopolymer A solvents. The nano-particles are simple models of proteins or colloids. We predict different vesicle structures, and relate these morphologies to particle size, distances between two particles, and volume fraction of the vesicles. It is found complex structures of the vesicle are induced by the twin particles: several or one reverse micelle surrounded by the outer monolayer; two micelles. These results are of immediate interest to the interactions of vesicles and particles, as well as to the transitions of vesicles to micelles.

1. Introduction

The interactions of nanoparticles with biological membranes have recently gained much interest among scientists in the field of nanotechnology [1–3]. As one of the major applications, nanoparticles can be designed to serve for drug delivery purposes by entering the target cell membrane and acting as drug containers [4]. The wrapping and internalization of nanoparticles by biomembranes plays a critical role in drug delivery applications and nanomedicine. Therefore it is crucial to understand the mechanisms by which nanoparticles interact with biological cells and enter the cell membrane [5–7].

Other example is the endocytosis. Endocytosis is a fundamental cellular process through which many artificial and natural biological objects are engulfed and internalized by the cell [8,9]. Wrapping and cellular uptake of technologically designed nanoparticles provides an important route to transport drug containers and deliver the cargo within the target cell. Cellular uptake of nanoparticles is associated with deformations induced on the plasma membrane of the cell by the particle.

While there are several simulations [10,6,11] and theoretical studies [12–18] about the interactions of a single nanoparticle with a vesicle, a comprehensive investigation on the effect of more than one particle is still missing. When more than one particle is adsorbed on a membrane, the interactions between the vesicle and particles become much more

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complicated. The geometry of the membrane is affected by the adsorbed particles. For a pair of particles encapsulated in a membrane, the shape deformations of the membrane depend on the relative distance between these particles. When particles come close together, they affect the adhesion area of one another.

In recent years, biomimetic polymer membrane [19,20], which is self-assembled from block copolymer amphiphiles, achieves a considerable success in experimental realization [21] or theoretical study of the natural biomembrane processes such as membrane fusions [22] and pores [23]. The membrane thickness can be increased up to 21 nm much larger than 3–5 nm for lipid membranes [24]. Indeed vesicles composed of diblock copolymers have been shown to exhibit behaviors similar to those of biological membranes [25].

Particularly, self-consistent theory is a powerful method taking into account entropy and enthalpic interaction. Our theoretical understanding can be built based on this well-tested model, which in many ways has provided useful insight into the fusion and fission of a membrane [22,26,27].

Despite all the studies in these research fields, it is still necessary for detailed understanding about the interactions of nanoparticles with vesicles. With this paper, we attempt to bring some ideas and conclusions that might be useful on the interactions of vesicles and particles.

2. Model and simulation details

The self-consistent field theory is used to study the formation of vesicles in a solution of an incompressible copolymer–homopolymer mixture. The system consists of n_a linear amphiphilic copolymers and n_s solvent molecules. The amphiphilic molecules are composed of A (hydrophilic) and B (hydrophobic) monomers, and the solvent molecules are represented by hydrophilic homopolymers consisting of A segments only. Each homopolymer and copolymer chain consists of N segments with a fixed monomer volume $1/\rho_0$. We assume that the A and B segments have the same segment length b. The dimensionless free energy of the system is given by Refs. [28–31]

$$\frac{NF}{\rho_0 k_B T V} = -\bar{\phi}_a \ln\Big(\frac{Q_a}{V\bar{\phi}_a}\Big) - \bar{\phi}_s \ln\Big(\frac{Q_s}{V\bar{\phi}_s}\Big) + \frac{1}{V}\int \mathrm{d}\boldsymbol{r}[\chi N\phi_h(\boldsymbol{r})\phi_t(\boldsymbol{r}) + \chi N\phi_s(\boldsymbol{r})\phi_t(\boldsymbol{r})] - \frac{1}{V}\int \mathrm{d}\boldsymbol{r}[w_h(\boldsymbol{r})\phi_h(\boldsymbol{r}) + w_t(\boldsymbol{r})\phi_t(\boldsymbol{r}) + w_s(\boldsymbol{r})\phi_s(\boldsymbol{r})] + \frac{1}{V}\int \mathrm{d}\boldsymbol{r}\xi(\boldsymbol{r})[\phi_h(\boldsymbol{r}) + \phi_t(\boldsymbol{r}) + \phi_s(\boldsymbol{r}) - \phi_0(\boldsymbol{r})]. \quad (1)$$

Here, the local volume fractions of A (head) and B (tail) segments of the amphiphiles are given by $\phi_h(\boldsymbol{r})$ and $\phi_t(\boldsymbol{r})$. Likewise, $\phi_s(\boldsymbol{r})$ is the local concentration of homopolymer solvent. The average volume fractions of amphiphilic copolymer and solvent homopolymer are $\bar{\phi}_a$ and $\bar{\phi}_s$, respectively. $w_h(\boldsymbol{r})$, $w_t(\boldsymbol{r})$, and $w_s(\boldsymbol{r})$ are the conjugate fields to the local volume fractions $\phi_h(\boldsymbol{r})$, $\phi_t(\boldsymbol{r})$, and $\phi_s(\boldsymbol{r})$, respectively, in a space point $\boldsymbol{r}$. k_B is the Boltzmann constant, and T is the absolute temperature. The hydrophobic and hydrophilic monomers interact with a local Flory–Huggins interaction repulsion parameter of strength χ, with a choice $\chi N = 30$. $\xi(\boldsymbol{r})$ is the Lagrange multiplier which enforces the incompressibility condition of the system. Q_s and Q_a are the single chain partition functions of the solvent and amphiphile molecules subjected to the above fields. V is the total volume of the system.

The surface of the particle is hard and impenetrable. The total segment density in the vicinity of its surface drops to zero in a boundary region of width ϵ according to Refs. [32–34]

$$\phi_0(\boldsymbol{r}) = \begin{cases} 0, & \boldsymbol{r} \le R, \\ \dfrac{1}{2}\left\{1 - \cos\left(\dfrac{\pi(\boldsymbol{r} - R)}{\epsilon}\right)\right\}, & R \le \boldsymbol{r} \le R + \epsilon, \\ 1, & \text{else.} \end{cases} \quad (2)$$

where ϵ is chosen much smaller than R_g, the polymer radius of gyration.

For simplicity, the nanoparticle is modeled with a neutral surface, not hydrophilic or hydrophobic.

Within the well established SCFT, the boundary conditions are needed. For the four boundaries of our simulation box, the Neumann condition is used. At the boundary on the particle, the Dirichlet condition is used, because of the hard particle surface and the polymer cannot cross the boundary.

To form the starting configuration, an equilibrated spherical "vesicle" is created by an artificially "biased" structure with two identical particles locating close in the center of the vesicle [22,35,36,33]. All the figures of vesicles in the paper are with the same size $40 \times 20\, R_g$. R_g is the gyration radius of the homopolymer chains. The radius of the particle is R.

3. Results

The shapes of the vesicle including particles have complex geometries. We choose three different cases, which predict the three probable morphology transformations of the vesicles in their interactions with twin enclosed particles. The parameters of the three systems are shown in Table 1.

The total free energies of the vesicles vary with the relative distances d between nanoparticles. d is the separation between centers of the two spherical particles. The free energies of the three different systems in Table 1 are shown in Figs. 1–3. The