Density functional simulations for self-assembling micellar structures in amphiphilic block copolymer solutions

Takashi Uneyama
JST-CREST, Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan
E-mail: uneyama@scl.kyoto-u.ac.jp

Abstract. Density functional simulations are performed to study various self-assembling micellar structures in amphiphilic block copolymer solutions. It was shown that onion structures (stacked multilayer structures) are formed when the hydrophilic interaction is weak. Simulation results imply that the onion structures are different from monolayer vesicle structures which is formed when the hydrophilic interaction is rather strong. The difference and similarity between the vesicle structures and onion structures, or between their kinetic formation pathways are discussed.

1. Introduction
It is known that block copolymers form various self-assembling micellar structures when dissolved in solvents [1]. For example, well-known micellar structures such as spheres, cylinders, or vesicles (closed bilayer structures) are formed spontaneously in amphiphilic block copolymer solutions. However, it is reported that more complicated micellar structures [2, 3] can be also formed by block copolymer solutions.

The morphologies of such self-assembling structures depend on various parameters such as the volume fraction of the polymers, the block ratio, or the solvent quality (strength of the interaction). Although many experiments [1] and simulations [4, 5] have been performed so far, the effects of these parameters on the resulting self-assembling structures are still not well understood.

In this work, the density functional simulations for amphiphilic block copolymer solutions were performed to study the effects of the interaction parameters. Special attention was payed on the effect of the strength of the solvophilic interaction. The difference and similarity between the onion structures (multilayer vesicle-like structures) and the single layer vesicle structures are then discussed. It is shown that they are qualitatively different while they share several common properties.

2. Model
We consider blends of amphiphilic AB diblock copolymers (which consists of the solvophilic A-subchain and the solvophobic B-subchain) and S solvents (the solvents are small molecules or polymers which have the selective interaction) as models of amphiphilic block copolymer solutions.
In this work, the density functional model for amphiphilic block copolymer solutions [6] is employed. In the density functional model, the state of the amphiphilic block copolymer solution is expressed by using three density fields $\rho_i(r)$ ($i = A, B, S$). The free energy of the system can be described as a functional of the density fields. The model free energy functional can be expressed as follows.

$$
\frac{F[\{\rho_i\}]}{k_B T} = \sum_{i,j=(A,B)} \int dr dr' 2 \sqrt{\int f_i f_j A_{ij} \tilde{G}(r-r')} \sqrt{\rho_i(r)\rho_j(r')}
+ \sum_{i=(A,B)} \int dr f_i C_{ii} \rho_i(r) \ln \rho_i(r) + \int dr C_{SS} \rho_S(r) \ln \rho_S(r)
+ \int dr 4 \sqrt{\int f_A f_B C_{AB} \rho_A(r)\rho_B(r)} + \sum_{i=(A,B,S)} \int dr \frac{b_i^2}{6} \left| \nabla \sqrt{\rho_i(r)} \right|^2
+ \sum_{i,j=(A,B,S)} \int dr \frac{\chi_{ij}}{2} \rho_i(r)\rho_j(r) + \int dr \frac{P(r)}{2} [\rho_A(r) + \rho_B(r) + \rho_S(r) - 1]
$$

where $b$ is the segment size, $f_i$ is the block ratio of the $i$-subchain, $A_{ij}$ and $C_{ij}$ are constants determined from $b$ and $f_i$. $\tilde{G}(r)$ is the nonlocal entropic interaction kernel which represents the effect of the connectivity between two blocks. $\chi_{ij}$ is the Flory-Huggins $\chi$ parameter between the $i$- and $j$-species, and $P(r)$ is the Lagrangian multiplier field which is determined to satisfy the incompressible condition $\rho_A(r) + \rho_B(r) + \rho_S(r) = 1$. For the time evolution, the following simple dynamic density functional equation [7] is assumed.

$$
\frac{\partial \rho_i(r,t)}{\partial t} = \nabla \cdot \left[ \frac{\rho_i(r)}{\zeta} \nabla \frac{\delta F[\{\rho_i\}]}{\delta \rho_i(r)} \right] + \xi_i(r,t)
$$

where $\zeta$ is the friction coefficient for a monomer (which is assumed to be the same for all the monomer species) and $\xi_i(r,t)$ is the thermal noise which satisfies the following fluctuation-dissipation type relation.

$$
\langle \xi_i(r,t) \rangle = 0, \quad \langle \xi_i(r,t)\xi_j(r',t') \rangle = -2\tilde{\beta}^{-1} k_B T \delta_{ij} \nabla \cdot \left[ \frac{\rho_i(r)}{\zeta} \nabla \delta(r-r') \right] \delta(t-t')
$$

Here, $\tilde{\beta}^{-1} \leq 1$ is the factor which determines the noise amplitude (the effective temperature of the noise reduces to $\tilde{\beta}^{-1} T$).

3. Simulations

So far, the density functional simulations for amphiphilic block copolymer systems with sufficiently strong solvophilic systems are performed [6,7]. For sufficiently solvophilic cases, it was shown that several well-known micellar structures can be actually formed and the morphologies depend on several parameters such as the volume fraction, the block ratio, or the interaction strength.

In this work, to consider the effect of hydrophilic interaction in more detail, simulations for not strong solvophilic interaction cases are performed. Thermodynamically stable structures can be directly obtained by minimizing the free energy (1) numerically (statics simulations). Dynamics simulations can be performed by solving the discretized version of eq (2) together with eq (1). It is empirically known that the resulting structures are qualitatively the same both for the static and dynamic simulations.

Snapshots for a typical dynamic simulation for a rather solvophobic interaction case are shown in Figure 1. The parameters for the simulation are as follows: the volume fractions...
\[ \bar{\rho}_{AB} = 0.2, \bar{\rho}_S = 0.8, \] the degrees of polymerization \( N_{AB} = 10, N_S = 10, \) the block ratios \( f_A = f_B = 0.5, \) and the \( \chi \) parameters \( \chi_{AB} = 1.75, \chi_{AS} = 0.5, \chi_{BS} = 2.5, \) the friction coefficient \( \zeta = 1, \) the temperature \( k_B T = 1, \) and the noise parameter \( \tilde{\beta}^{-1} = 0.04. \) The initial condition (at \( t = 0 \)) is the homogeneous state and the system size is \( 24 \times 24 \times 24 \) (periodic boundary condition). The time step size is \( \Delta t = 0.0025 \) and the lattice size is \( \Delta x = 0.5. \) The simulation is performed from \( t = 0 \) to \( t = 3125. \)

From Figure 1, it can be observed that small micellar structures are formed rapidly from the homogeneous initial state (Figure 1 (a),(b)), and the structures slowly grow into multilayer onion structures mainly by collision of small structures (Figure 1 (c),(d)). The observed structures look similar to ones obtained by the self consistent field simulations for diblock copolymer solutions [8].

![Figure 1](image)

**Figure 1.** Snapshots of the dynamic density functional simulation for the onion structure formation. Grey and black surfaces mean the isodensity surfaces for solvophilic and solvophobic blocks \( (\rho_A(r) = 0.5 \) and \( \rho_B(r) = 0.5) \), respectively. (Solvents are not explicitly shown.) The time for each snapshot corresponds to (a) \( t = 6.25, \) (b) \( t = 62.5, \) (c) \( t = 625, \) and (d) \( t = 3125. \)

### 4. Discussions

From the previous simulation results [6, 7], we find that spherical micelles, cylindrical micelles, and bilayer vesicles are formed when the solvophilic interaction is strong. The simulation results by this work implies that onions (multilayer vesicle-like structures) are formed when the solvophilic interaction is weak or the block copolymer is solvophobic. Also we find that the formation pathway of the onion structures is different from one of the vesicle structures. In the vesicle formation case, first, small micellar structures are formed from the homogeneous initial state. Then small structures grow into micellar bilayer structures by collisions, and finally bilayer structures are closed to form vesicles. This is the conventional vesicle formation process [9] and is also observed in particle simulations [4, 10].

In the onion formation case, the early stage is almost the same as the vesicle formation case. Small micellar structures are formed from the homogeneous state. The small structures grow into larger droplet like structures by collisions. Layer structures are rearranged in the droplets and thus multilayer structures are formed. Onion structures become larger by further collisions and rearrangements. Also, structures can grow by the evaporation-condensation (or the Ostwald ripening) type process. (Both the collision-rearrangement and evaporation-condensation growth processes are slow.) It will be reasonable to consider that the onion structures are microphase separation structures in block copolymer rich droplets [2] rather than usual micellar structures. This will be a natural interpretation because the micellar structures (or the block copolymer rich domains) always have spherical droplet like shapes, and there is rather strong interfacial energy between the micellar droplet phase and the outer solvent phase. In fact, we obtain packed...
cylinder like structures in droplet like regions if we change the block ratio. These results are consistent with the simulation results by other continuum field models [8,11].

Therefore, the two formation pathways are different in the late stage while they are quite similar in the early stage. These formation pathways are schematically shown in Figure 2. While the pathways are different, there are still similarity between two cases even in the late stage. Each structure has closed spherical shell like structures and they are formed from disk like layer structures. The layer closure processes look quite similar for two cases. The layers have bending energy, and the closure processes are driven by other thermodynamic forces. For the vesicle formation case, the driving force is the line tension energy at the bilayer edges [9]. However, for the onion formation case, it will be reasonable to consider that the driving force is the surface energy of the micellar droplets because the shapes of droplets are always kept to be spherical and the contribution of the line tension energy is generally not large for relatively small structures. Thus the driving forces of the structure formations are different for two processes. This is consistent with the fact that the characteristic size of monolayer onion structures is smaller than one of the vesicles because the contribution of the surface energy is strong even for small structures, compared with the line tension energy.

![Figure 2](image.png)

Figure 2. Schematic draw of the formation pathways of a monolayer vesicle and a multilayer onion. Grey and black colors mean the solvophilic and solvophobic subchains, respectively. The upper pathway corresponds to the strongly solvophilic systems whereas the lower pathway corresponds to the weakly solvophilic or solvophobic systems.

5. Conclusion

The density functional simulations for amphiphilic block copolymer solutions were performed with various solvophilic interaction strengths. It was shown that when the solvophilic interaction is weak or the block copolymer is solvophobic, stacked multilayer onion structures are formed instead of well-known micellar structures such as vesicles. We found that the formation pathway of the onion structures is different from one of the vesicles, and discussed the difference and similarity between them. To make the difference and similarity clearer we will need to perform simulations with various interaction parameters and discuss thermodynamic properties in more detail. Further investigation will be the subject of future work.

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