Stable Phase of Diblock Polymer Using SCFT in Real Space in 2D and 3D

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Abstract: *A numerical method in real-space is developed to solve the polymeric self-consistent field equations. In this report, we apply our method to AB linear diblock copolymer melt, thus reproduce stable phase "lamellae" which is the simplest ordered phase and have comparable volume fractions of both polymers. We also reproduce "cylinder (hexagonal in 2D) phases" for noncomparable volume fractions of both the polymers. Also pseudo-spectral method is used which uses Fourier space and has higher accuracy than central difference differentiation method. The calculation area used in method to solve stability of phase is a cube in 3D.*

1. Introduction

Diblock polymers can be assembled to various ordered structures, which is favoured because it helps to avoid energetically unfavourable contacts between A and B polymer molecule. Various ordered structures are formed depending on the volume fractions of the monomers present. We get cubic, hexagonal, gyroid, double diamond, catenoid lamellae, and many others beside lamellae. SCFT is a big tool for studying these equilibrium phase behaviour of block copolymers. By searching for the solutions of the self-consistent field equations, we can find the equilibrium ordered patterns of diblock copolymer. We apply SCFT equations to solve for the stable lamellae phase which is rich in both A and B (in terms of volume fractions). Since solving SCFT is not trivial as it involves a lot of non-linear

equations, iterative and convergence methods are used to find the solutions of stable phase. Prior information regarding states is not required to find the stable phases but to accelerate convergence of iterative methods, we use some known initial values of fields of the phase. It can be noted that the patterns in stable block copolymers exhibit periodic symmetry. We carry out our method to get convergent free energy of diblock copolymer according to SCFT which does signify the stability of phase.

2. Problem Formulation

First let us write out main equation that we are trying to solve and then expain terms and how to get to these terms. The free energy density is given by

$$F = \frac{1}{V} \int (\chi_{AB}\phi_A\phi_B - \omega_A\phi_A - \omega_B\phi_B - X_i(1 - \phi_A - \phi_B))dr - \log Q \tag{1}$$

where χ_{AB} is the FloryHuggins segment segment interaction parameter, $\omega_A(r)$, $\omega_B(r)$ are the external fields, which act on A and B monomers respectively. The normalized segment density operators are φ_A and φ_B at r. X_i is the deviation that we get in unstable state as there is some non-zero value in $\varphi_A + \varphi_B - 1$. Q is the single-chain partition function, which is determined by

$$Q = \frac{1}{V} \int q(r,1)dr \tag{2}$$

The forward propagator q(r,s) represents the probability density that the chain of contour length s has its end at position r, where the variable s is used to parameter each copolymer chain, s = 0 represents the tail of the A block and s = f is the junction between the A and B blocks. A-monomer fraction is f. Correspondingly, the B-monomer fraction is 1 - f. q satisfies the modified diffusion equation,

$$MDE = \frac{\partial q}{\partial s} = N\left(\frac{1}{6}\nabla^2 q - \omega q\right) \tag{3}$$

where N is the total degree of polymerization of diblock copolymer. The respective external field acting on the blocks and deviation are given by

$$\omega_A = \omega_A + \lambda(\chi AB\varphi_B - \omega_A + X_i) \tag{4}$$

$$\omega_B = \omega_B + \lambda(\chi AB\varphi_A - \omega_B + X_i) \tag{5}$$

$$X_i = X_i + \lambda(\varphi_A + \varphi_B - 1) \tag{6}$$

where λ is the mixing parameter and is usually taken to be less then 0.1. We combine these external fields ω_A and ω_B to easily solve MDE.

$$\omega = \omega_A \quad \text{for} \quad 0 \le s \le f \tag{7}$$

$$\omega = \omega_B \quad \text{for} \quad f < s \le 1 \tag{8}$$

The above relation is opposite for qd(r,s) which is the reverse propagator. At s=0, both q and qd have value 1 at all r as probability at s=0 is 1.

$$q(r,0) = 1 \tag{9}$$

$$qd(r,0) = 1 \tag{10}$$

φ_A and φ_B are given by:

$$\phi_A = \frac{V}{Q} \int_0^f q(r,s) \times qd(r, 1-s)ds \tag{11}$$

$$\phi_B = \frac{V}{Q} \int_f^1 q(r,s) \times qd(r, 1-s)ds \tag{12}$$

3. Numerical Method

We first start with close initial value approximation of ω_A and ω_B of lamellae state. Then we solve the modified diffusion equation using pseudo spectral method which changes the equation into simply

$$qn+1 = R\Delta s \times qn \tag{13}$$

where $R_{\Delta s}$ is

$$R_{\Delta s} = e^{-\frac{\omega \Delta s}{2}} \times e^{\Delta s \nabla^2} \times e^{-\frac{\omega \Delta s}{2}} \qquad (14)$$

We calculate fourier transform using FFT of first exponent and multiply with the corresponding fourier transform of the 2nd exponent. Then we take inverse fourier transform of product and multiply with the third exponent to get $R\Delta s$ and thus q_{n+1}. Once we get new q, we substitute it in φ equations and get the respective φ. Then we calculate free energy. This completes first iteration. To get new ω_A and ω_B we use the respective equations given above and carry out the above operations to get free energy again. Thus, when free energy converges we can be convinced that a particular stable state is found. Since the solution is periodic we use boundary conditions in which the value of q at a particular s is same at boundaries, i.e., q at r=L+1 is equal to q at r=1; where r=1 signifies x=y=z=1 and L is the end of a particular dimension. We repeated the same for the cylinder (hexagonal in 2D) phase.

4. Results and Discussion

The algorithm described above has been applied to a diblock copolymer melt and the random sinusoidal variation to calculate initial value of ω results in finding the stable phase of lamellae easily. Although it can also be found that if we take any other initial approximation the method works but our chosen initial approximation helps to accelerate the convergence. To see the result of our method, if we plot the values of the average volume density of one of the polymer we see that alternating stripes of band involving high and low density of one of the polymer are observed. The advantage of our method over Matsen-Schick's method is that Matsen-Schick's method cannot be used to discover new patterns straightforwardly. Our strategy only needs to add a little symmetric information into the initial estimation. It is more adaptive and flexible for discovering new patterns with less computational effort. Also, the use of pseudo spectral method of RK2 involves the symmetric breakup of the ω operator which in turn ensures RK2 that odd powers of the global error are eliminated. Also our method is far more accurate in calculating q than central difference differentiation. (a) lamellae(2D) (b) lamellae(3D)
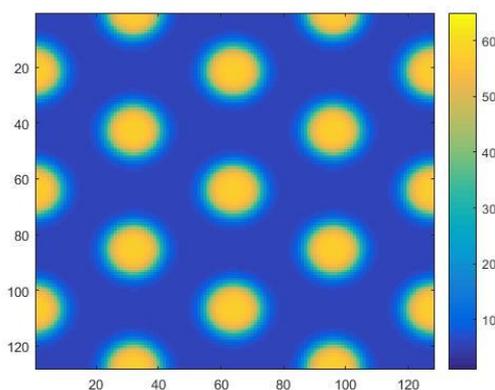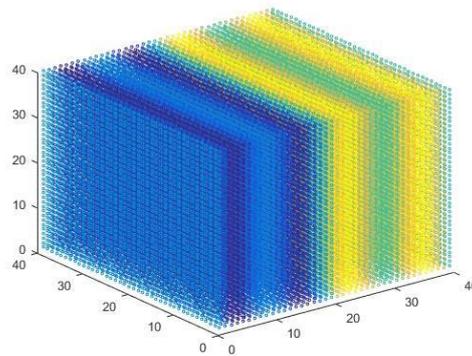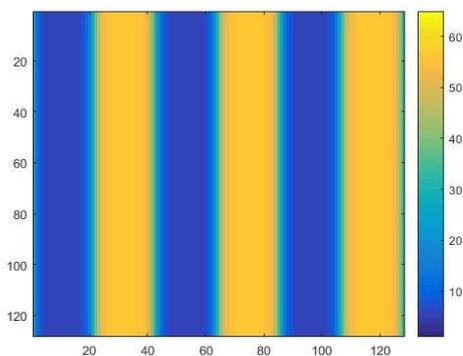
(c) Hexagonal (2D)
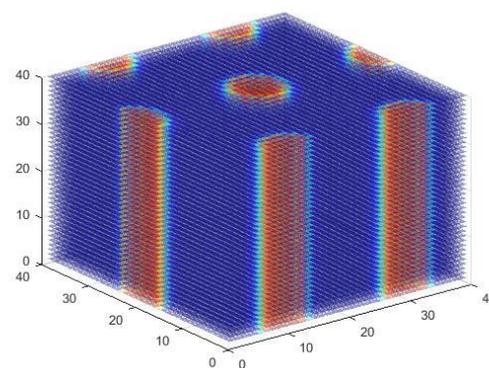
(d) Cylinder (3D)

5. Path Forward

The future work includes application of this method to triblock polymers, improving convergence by use of anderson mixing rather than simple mixing in calculation of ω, use of CGF4 algorithm (developed by Cochran, Garca-Cervera and Fredrickson) or extension of RK2 to fourth-order using Richardson extrapolation to calculate q. Also, the behavior of nano particles can be examined.

6. Conclusion

A numerical method which does not need a priori symmetric information and solves the SCFT based on real space whose calculation area is cubic in 3D is developed. The method is applied to diblock copolymer system. As mentioned earlier, the SCFT equations are nonlinear system and have multiple solutions. An efficient method for estimating optimized initial values of lamellae and cylinder (hexagonal in 2D) phase is given. Using that method, we calculated stable

lamellae and cylinder (hexagonal in 2D) phases of diblock copolymer. We also used simple mixing to calculate external fields which fastens convergence. Numerical examples demonstrate that our method has some advantages over the one which uses central difference differentiation to calculate MDE.

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