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Self-consistent field theory simulation of block copolymer films adsorbed on surfaces of azimuthally symmetric particles

S V Lishchuk

Materials and Engineering Research Institute, Sheffield Hallam University, Howard Street, Sheffield, S1 1WB, UK

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Abstract

A method is proposed for solving self-consistent field theory equations for thin block copolymer films adsorbed on a surface of axially symmetric particles. The method is applied to the case of thin diblock copolymer film adsorbed on a prolate spheroidal particle. Two-dimensional analogues of lamellar and cylindrical morphologies are observed.

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1. Introduction

There is growing scientific interest in the properties of block copolymer nanoshells and block copolymer films adsorbed on nanoparticles. These systems have a range of promising applications due to ease of control of their structure and properties [1–7]. Currently experimental techniques have become available for polymer encapsulation of particles [8–13] and subsequent removal of the particle template to form polymer capsules [14, 15].

Although the particles typically used in current experimental and theoretical studies are spherical, several methods have been recently developed to obtain particles with well-controlled anisotropic shapes [16–19], and such particles have now become available commercially. The use of computer modelling is important for predicting the behaviour of block copolymer films adsorbed on anisotropic particles.

One of the most successful tools for modelling polymer fluids and other soft condensed matter systems in general, and block copolymer nanoshells in particular, is self-consistent field theory (SCFT) [20, 21]. In SCFT the functional integrals of a statistical field theory of inhomogeneous polymers are evaluated in the mean-field approximation [20, 22, 23]. In the case of block copolymers SCFT provides a description of a rich variety of observed phases as well as prediction of new morphologies.

The main quantity calculated in SCFT is the probability distribution function $q(\mathbf{r}, s)$ which gives the probability of finding polymer segment s at position \mathbf{r} . This quantity satisfies

a modified diffusion equation, the numerical solution of which is the most time-consuming part of modelling. As a result, SCFT is most efficient for modelling copolymer melt films in flat space [24, 25].

Two works have appeared recently that extend SCFT to spherical geometry and apply it to the study of the two-dimensional microphase separation of block copolymer on a sphere. Li *et al* [26] solve the modified diffusion equation in real space by discretizing a sphere and employing the representation of the Laplace operator on the resulting mesh. Then the modified diffusion equation is solved using a second-order accurate alternate-direction implicit (ADI) algorithm. On the other hand, Chantawansri *et al* [27] address the problem by representing the probability distribution function in the basis of spherical harmonics. This has allowed construction of an efficient second-order accurate scheme which utilizes the advantage of the Laplace operator having the diagonal form in the spherical harmonics basis, and the efficiency of fast Fourier transform (FFT) method.

This paper presents a modification of the method by Chantawansri *et al* [27] for solving self-consistent field theory equations for a thin block copolymer films adsorbed on a surface of axially symmetric particles homeomorphic to a sphere. The method is illustrated by considering the case of a thin diblock copolymer film adsorbed on a prolate spheroidal particle.

2. Self-consistent field theory on a sphere

In this section we outline the standard framework of the self-consistent field theory [23, 20, 27] and the pseudospectral method for the solution of the modified diffusion equation on a sphere [27].

2.1. SCFT framework

The standard framework of SCFT consists in obtaining mean-field configurations of the auxiliary Hubbard–Stratonovich fields [23, 20, 27]. For the case of the incompressible AB diblock copolymer melt these fields are the pressure field $\Xi(\mathbf{r})$ and the composition field $W(\mathbf{r})$. The partition function of the system can be written as the functional integral

$$Z = \int \mathcal{D}\Xi \mathcal{D}W e^{-\mathcal{H}[\Xi, W]}. \quad (1)$$

The mean-field configurations of these fields correspond to the saddle point of the effective Hamiltonian $\mathcal{H}[\Xi, W]$ given by the equations

$$\frac{\delta \mathcal{H}[\Xi, W]}{\delta \Xi(\mathbf{r})} = 0, \quad \frac{\delta \mathcal{H}[\Xi, W]}{\delta W(\mathbf{r})} = 0, \quad (2)$$

which can be explicitly written as [27]

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) - 1 = 0 \quad (3)$$

and

$$(2f - 1) + \frac{2W(\mathbf{r})}{\chi N} - \phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 0. \quad (4)$$

Here f is the volume fraction of A monomers in the diblock, χ is the Flory–Huggins parameter and N is the degree of polymerization. The local volume fractions of A and B monomers, ϕ_A and ϕ_B , are calculated as

$$\phi_A(\mathbf{r}; [\Xi, W]) = \frac{1}{Q} \int_0^f q_A(\mathbf{r}, s) q_B(\mathbf{r}, 1 - s) ds, \quad (5)$$

$$\phi_B(\mathbf{r}; [\Xi, W]) = \frac{1}{Q} \int_f^1 q_A(\mathbf{r}, s) q_B(\mathbf{r}, 1-s) ds, \quad (6)$$

where

$$Q[\Xi, W] = \frac{1}{V} \int_V q_A(\mathbf{x}, 1; [\Xi, W]) d\mathbf{r} \quad (7)$$

is the partition function of a single AB diblock copolymer interacting with the external field and $q_\alpha(\mathbf{r}, s; [\Xi, W])$, $\alpha = A, B$, are end-segment distribution functions [23], also referred to as restricted partition functions [20], or forward and backward propagators [27].

The end-segment distribution functions $q_\alpha(\mathbf{r}, s)$ satisfy the modified diffusion equation

$$\frac{\partial q_\alpha(\mathbf{r}, s)}{\partial s} = \nabla^2 q_\alpha(\mathbf{r}, s) - \psi_\alpha(\mathbf{r}, s) q_\alpha(\mathbf{r}, s), \quad (8)$$

with the initial condition $q_\alpha(\mathbf{r}, 0) = 1$. The fields $\psi_\alpha(\mathbf{r}, s)$ are given by

$$\psi_A(\mathbf{r}, s) = \begin{cases} \Xi(\mathbf{r}) - W(\mathbf{r}), & 0 < s < f \\ \Xi(\mathbf{r}) + W(\mathbf{r}), & f < s < 1 \end{cases} \quad (9)$$

and

$$\psi_B(\mathbf{r}, s) = \begin{cases} \Xi(\mathbf{r}) + W(\mathbf{r}), & 0 < s < 1-f \\ \Xi(\mathbf{r}) - W(\mathbf{r}), & 1-f < s < 1. \end{cases} \quad (10)$$

2.2. Modified diffusion equation on a sphere

The most computationally expensive step in the SCFT algorithm is the solution of the modified diffusion equation (8). An efficient scheme for this purpose is based on the pseudospectral operator splitting method [28]. In this method the formally exact solution of equation (8),

$$q_\alpha(\mathbf{r}, s + \Delta s) = \exp\{ds[\nabla^2 - \psi_\alpha(\mathbf{r}, s)]\} q_\alpha(\mathbf{r}, s), \quad (11)$$

is transformed using the Baker–Hausdorff formula [29] to the form

$$\begin{aligned} q_\alpha(\mathbf{r}, s + \Delta s) &= \exp\left[-\frac{\Delta s}{2} \psi_\alpha(\mathbf{r}, s)\right] \exp[\Delta s \nabla^2] \\ &\times \exp\left[\frac{\Delta s}{2} \psi_\alpha(\mathbf{r}, s)\right] q_\alpha(\mathbf{r}, s) + \mathcal{O}(\Delta s^3). \end{aligned} \quad (12)$$

The differential operator $e^{\Delta s \nabla^2}$ can be applied as a multiplication in the basis of Laplacian eigenfunctions. This is achieved by the Fourier transform of $q_\alpha(\mathbf{r}, s)$ in the flat space [28], or by spherical harmonic expansion on the surface of a sphere [27].

Below we outline the spherical harmonic expansion for further reference. The spherical harmonic expansion of a function $q(\mathbf{r}) \equiv q(\theta, \varphi)$ defined on a sphere, θ and φ being spherical coordinates, is defined by

$$q(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \hat{q}_l^m Y_l^m(\mathbf{r}), \quad (13)$$

where

$$Y_l^m(\mathbf{r}) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\varphi} \quad (14)$$

are the spherical harmonics of degree l and order m , $P_l^m(\cos \theta)$ are the associated Legendre polynomials. The coefficients \hat{q}_l^m are given by the integral over a sphere:

$$\hat{q}_l^m = \int_{S^2} q(\mathbf{r}) \bar{Y}_l^m(\mathbf{r}) d\mathbf{r}, \quad (15)$$

$\bar{Y}_l^m(\mathbf{r})$ being the complex conjugate of $Y_l^m(\mathbf{r})$. The Laplacian of the spherical harmonic is

$$\nabla^2 Y_l^m(\mathbf{r}) = -\frac{l(l+1)}{R^2} Y_l^m(\mathbf{r}). \quad (16)$$

The differential operator $e^{\Delta s \nabla^2}$ can be written in the spherical harmonic basis as a numerical factor:

$$e^{\Delta s \nabla^2} Y_l^m(\mathbf{r}) = \exp\left[-\frac{l(l+1)}{R^2} \Delta s\right] Y_l^m(\mathbf{r}). \quad (17)$$

3. Modified diffusion equation on surfaces of revolution

The spherical harmonic expansion (13) can be formally applied to the function $q(\mathbf{r})$ defined on an arbitrary surface diffeomorphic to a 2-sphere. This, in principle, allows one to use the operator splitting method, equation (12), for solving the modified diffusion equation on such surfaces. However, spherical harmonics are generally not the eigenfunctions of the Laplacian, and the spherical harmonic expansion (13) of the Laplacian of the spherical harmonic contains off-diagonal terms. This makes computation of the operator $e^{\Delta s \nabla^2}$ rather expensive, and thus the advantages of the pseudospectral method are lost. One approach to the problem could consist in replacing the spherical harmonic basis by the basis of the Laplacian eigenfunctions for a given surface. The computation of such a basis is in general a rather difficult task.

In the present paper we consider surfaces of revolution and propose to continue to use spherical harmonic basis for such surfaces. It is shown below that azimuthal symmetry of such surfaces leads to significant reduction in the amount of computation of the operator $e^{\Delta s \nabla^2}$. This, in conjunction with the possibility of using fast Fourier transforms on azimuthally symmetric surfaces, results in comparatively fast algorithm for solving the modified diffusion equation and, conveniently, allows one to apply small modifications to existing codes intended for solving SCFT equations on the sphere to adapt them for the case of block copolymer films adsorbed on arbitrary surfaces of revolution.

This section describes the general method and demonstrates its applicability on the case of a thin diblock copolymer film adsorbed on the surface of the prolate spheroidal particle.

3.1. General method

We consider a thin block copolymer film adsorbed on a particle the surface of which is a smooth surface of revolution diffeomorphic to 2-sphere. Prolate and oblate spheroids, pear- and dumbbell-shaped particles are typical examples of such surfaces.

The standard parametrization of a surface of revolution is given by

$$\begin{aligned} x(\theta, \varphi) &= \rho(\theta) \cos \varphi, \\ y(\theta, \varphi) &= \rho(\theta) \sin \varphi, \\ z(\theta, \varphi) &= z(\theta), \end{aligned} \quad (18)$$

where the Cartesian coordinates x, y, z of a surface are functions of the polar angle φ and the coordinate θ . The curvilinear system of coordinates (θ, φ) is orthogonal with the scale factors

$$h_\theta = \sqrt{\rho'^2(\theta) + z'^2(\theta)}, \quad h_\varphi = \rho(\theta), \quad (19)$$

and an area element

$$dS = h_\theta h_\varphi = \rho(\theta) \sqrt{\rho'^2(\theta) + z'^2(\theta)}. \quad (20)$$

The Laplacian is given by the expression

$$\nabla^2 = \frac{1}{h_\theta^2} \left[\frac{\partial^2}{\partial \theta^2} + \frac{d \ln(h_\varphi/h_\theta)}{d\theta} \frac{\partial}{\partial \theta} \right] + \frac{1}{h_\varphi^2} \frac{\partial^2}{\partial \varphi^2}. \quad (21)$$

Due to the azimuthal symmetry of the surface, the polar angle φ enters the expression for the Laplacian, equation (21), as a term $\partial^2/\partial\varphi^2$ with a factor $1/h_\varphi^2$ independent of φ . As a result, the Laplacian of the spherical harmonic of order m can be expanded in spherical harmonics of the same order:

$$\nabla^2 Y_l^m(\mathbf{r}) = \sum_{l'=m}^{\infty} \hat{b}_{l'}^m Y_{l'}^m(\mathbf{r}). \quad (22)$$

Consequently, the matrix of the Laplacian in the spherical harmonic basis, L , is block diagonal, thus significantly reducing the amount of the computation required to calculate the Laplacian. The coefficients $\hat{b}_{l'}^m$ are given by

$$\hat{b}_{l'}^m = \int_S \nabla^2 Y_l^m(\mathbf{r}) \bar{Y}_{l'}^m(\mathbf{r}) \, d\mathbf{r}, \quad (23)$$

the integration being taken over the surface.

Diagonalizing the Laplacian matrix

$$L = P^{-1} A P, \quad (24)$$

where A is a diagonal matrix with the eigenvalues of L , and P is an invertible matrix of the corresponding eigenvectors, we can represent the operator $e^{\Delta_s \nabla^2}$, which enters equation (12), in the form

$$e^L = P^{-1} e^A P. \quad (25)$$

Effectively, equation (25) provides transformation to the basis of the eigenfunctions of the Laplace operator on the given surface. Since for a given geometry the Laplacian matrix L is known in advance, the transformation matrix P , which enters equation (24), and its inverse can be pre-computed for subsequent use in the operator-splitting method using well-known spectral decomposition techniques [30].

As a result, the azimuthal symmetry of the surface allows one to obtain an efficient algorithm for solving the modified diffusion equation by taking advantage of fast Fourier transform in the polar angle φ , and single summation in the spherical harmonic expansion of the Laplacian, equation (22). The efficiency of the calculation can be further improved by employing fast methods for spherical harmonic expansion (e.g. [31–34]) and matrix multiplication (e.g. [35, 36]).

3.2. Example: prolate spheroids

In this subsection we demonstrate the validity of the method described above by its application to the case of the thin diblock copolymer film adsorbed on the surface of the prolate spheroidal particle. The natural choice for parametrization of the surface of prolate spheroid is provided by prolate spheroidal coordinates.

Different definitions of prolate spheroidal coordinates exist in the literature [37–41]. We choose prolate spheroidal coordinates (θ, φ) defined as

$$\begin{aligned} x &= a \sinh \mu \sin \theta \cos \varphi, \\ y &= a \sinh \mu \sin \theta \sin \varphi, \\ z &= a \cosh \mu \cos \theta. \end{aligned} \quad (26)$$

The parameters a and μ set the equatorial radius

$$R = a \sinh \mu, \quad (27)$$

and the aspect ratio (the ratio of the polar and equatorial diameters)

$$A = \coth \mu \quad (28)$$

of the prolate spheroid. The scale factors and the area element are respectively given, according to equations (19) and (20), by the following expressions:

$$h_\theta = a \sqrt{\sinh^2 \mu + \sin^2 \theta}, \quad (29)$$

$$h_\varphi = a \sinh \mu \sin \theta, \quad (30)$$

$$dS = a^2 \sinh \mu \sin \theta \sqrt{\sinh^2 \mu + \sin^2 \theta}. \quad (31)$$

The Laplacian in prolate spheroidal coordinates, following equation (21), has the form

$$\nabla^2 = \frac{1}{a^2(\sinh^2 \mu + \sin^2 \theta)} \left[\frac{\partial^2}{\partial \theta^2} + \frac{\sinh^2 \mu \cot \theta}{\sinh^2 \mu + \sin^2 \theta} \frac{\partial}{\partial \theta} \right] + \frac{1}{a^2 \sinh^2 \mu \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}. \quad (32)$$

The spherical harmonics defined in prolate spheroidal coordinates coincide with the angular part of the prolate spheroidal harmonics [40]. Application of the Laplace operator (32) to the spherical harmonic $Y_l^m(\theta, \varphi)$ yields

$$\begin{aligned} \nabla^2 Y_l^m(\theta, \varphi) = & - \left[\frac{l(l+1) + \frac{m^2}{\xi^2 - 1}}{a^2(\xi^2 - \eta^2)} - \frac{(l+1)\eta^2}{a^2(\xi^2 - \eta^2)^2} \right] Y_l^m(\theta, \varphi) \\ & - \sqrt{\frac{(2l+1)[(l+1)^2 - m^2]}{2l+3}} \frac{\eta}{a^2(\xi^2 - \eta^2)^2} Y_{l+1}^m(\theta, \varphi), \end{aligned} \quad (33)$$

with $\xi \equiv \cosh \mu$ and $\eta \equiv \cos \theta$. The expressions for the coefficients \hat{b}_{ll}^M are found by substituting equation (33) into equation (23).

Precalculation of the block-diagonal Laplacian matrix, consisting of coefficients \hat{b}_{ll}^M and the block-diagonal transformation matrix P , which enters equation (25), allows one to implement an efficient scheme for solving the modified diffusion equation on the prolate spheroid. Note that direct use of the basis of Laplacian eigenfunctions on a prolate spheroid would require calculation of prolate spheroidal wavefunctions which is known to be a difficult task [42–45].

We have implemented the SCFT algorithm, outlined in section 2 and described in detail in [27], for the case of thin diblock copolymer film on the surface of the prolate spheroid. The principal difference compared to the case of the spherical surface consists in using equation (25) together with equations (22), (23) and (33) for evaluation of the Laplacian exponential. Although the integrals (23) can be calculated analytically, the result is rather complicated, and we have found numerical integration more efficient. Another difference from the case of the spherical geometry consists in using the area element (31), corresponding to prolate spheroidal coordinates, in all integrations over the surface.

Evenly spaced grid in the coordinates θ and φ was used:

$$\theta_i = \frac{\pi i}{N-1}, \quad i = 0, \dots, N-1, \quad (34)$$

$$\varphi_j = \frac{2\pi j}{N-1}, \quad j = 0, \dots, N-1. \quad (35)$$

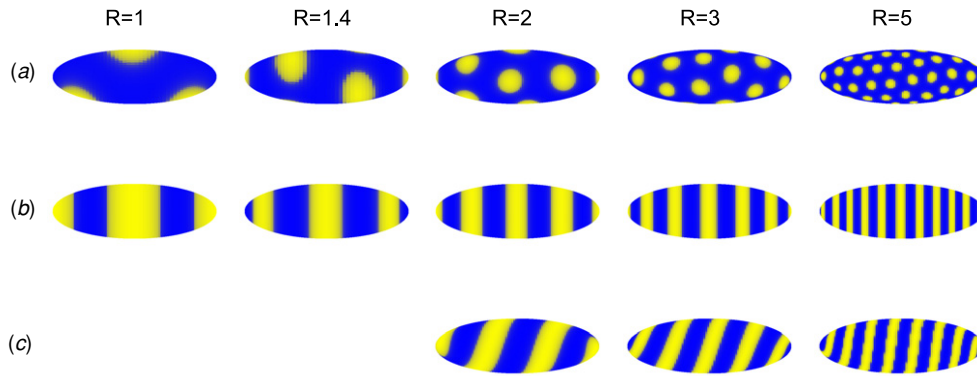


Figure 1. Composition profile of a thin diblock copolymer film with $\chi N = 25$ adsorbed on the surface of the prolate spheroid with the aspect ratio $A = 3$ and different equatorial radii R . We observe a 2D cylindrical phase at $f = 0.3$ (a), and different lamellar phases at $f = 0.5$ (b,c).

(This figure is in colour only in the electronic version)

The total number of grid points in the θ and φ directions, $N = 64$, the values of the discretization step of the chain contour variable $\Delta s = 0.05$ and the SCFT time step $\Delta t = 1.0$ were chosen to ensure that the finer discretization does not change the observed microphase separation patterns.

Several simulations were performed for the prolate spheroids of different equatorial radii R and the aspect ratio $A = 3$. Figure 1 presents different morphologies corresponding to different values of the volume fraction of A monomers in the diblock f . We observe 2D cylindrical ('spot', figure 1(a)) and lamellar ('hedgehog', figure 1(b), and 'spiral', figure 1(c)) morphologies which are analogous to those found in spherical, cylindrical and flat geometries. The figures for $R = 1$ and $R = 1.4$ are missing in part (c) of figure 1 because no stable 'spiral' morphologies were observed in these cases.

4. Conclusion

A method has been proposed for solving SCFT equations for thin block copolymer films adsorbed on a surface of axially symmetric particles. The key idea lies in solving the modified diffusion equation for the polymer segment probability distribution function in the basis of spherical harmonics. This allows one to retain the efficiency of the pseudospectral method while increasing the range of particle shapes that can be investigated.

The method has been applied to the case of thin diblock copolymer film adsorbed on a prolate spheroidal particle and two-dimensional analogues of lamellar and cylindrical morphologies are observed. Note that the purpose of the present study was to illustrate the validity of the method rather than to attempt finding configurations which correspond to the global minimum of the free energy of the system; therefore, we do not claim to span the whole configuration space. Nevertheless, the similarity of the morphologies observed on the prolate spheroidal surface to those observed previously in simpler geometries makes this approach a promising modification of the SCFT simulation method.

Systematic application of the presented method to thin block copolymer films adsorbed on azimuthally symmetrical particles should allow construction of detailed phase diagrams of these systems in the space of the parameters such as composition of block copolymer and

interaction between blocks, and thus help in guiding experimental investigation and possible application of anisotropic block copolymer nanoshells.

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