Confined Copolymer Structures

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Abstract. Bulk morphologies of diblock copolymers have been extensively studied in literature both experimentally and theoretically. Depending on the composition of the blocks it is comprised of, the bulk structures correspond to lamellae, gyroids, cylinder hexagonal arrangements and BCC structures of spheres. Recent research has shown that confinement is a powerful tool to break the symmetry of a structure, and obtain new shapes, different from those of the bulk. The process of forming new morphologies by confinement in nano-droplets, created from a dewetting process, was simulated. The structures obtained showed a great similarity with the experimental results present in the literature. The developed model captures the fundamental interactions that determine the dynamics of the phase separation process of the confined copolymer system between a rigid substrate and a free surface.

1. Introduction

The dewetting process is a phenomenon that occurs on a liquid film. Starting from a homogeneous film deposited on a substrate, the process of dewetting has as a result the rupture of the film and the droplet arrangements formation [1].

Generally, the film is prepared by spin-coating and deposited on a flat substrate. During the annealing process, the surface of the polymer is dominated by thermally excited waves. The thermally induced z-modulations on the liquid surface are modelled with the expression

\[ z(\vec{r}, t) = h + \delta h \exp[i \vec{q} \cdot \vec{r}] \]  \hspace{1cm} (1)

Here, \( h \) is the initial film thickness.

With

\[ \delta h = \delta h_0 \exp \left[ t / \tau_q \right] \]  \hspace{1cm} (2)

Where \( \tau_q \) represents the relaxation time of the \( q \) modes presented by the disturbance. Following the spinodal decomposition dynamics, the disturbances are amplified exponentially if they are less than a critical \( q_c \)-value. The fastest growing mode is:

\[ q_m = \sqrt{3/2} \frac{a}{h^2} \]  \hspace{1cm} (3)

With \( h \) as the initial film thickness and \( a \) as the molecular size.

The maximum fluctuation has a characteristic time:

\[ \tau_{q_m} = \frac{\pi \eta \eta}{\delta a} \]  \hspace{1cm} (4)
With $\eta$ the viscosity and $\gamma$ the superficial tension. For example, in a polyethylene film [1] a typical value is $\eta \approx (1 - 10) \times 10^6 \text{m}^{-1}$.

Instabilities cause the film to break at some points on the surface. Once the film breaks, the holes will grow proportionally to time $t$, where $R$ represents the size of the average size of the holes. The evolution and collision of the holes, transforms the film into a boundary Voronoi structure. During the subsequent evolution, the approximately toroidal boundaries decrease in a crown-shape of isolated droplets. The rupture of the boundaries is due to Rayleigh instabilities.

The droplet final shape presents a contact angle determined by Young’s law

$$\cos(\theta) = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$

Where $\gamma_{sg}$, $\gamma_{sl}$ and $\gamma_{lg}$ represent superficial tensions between solid-gas, solid-liquid and liquid-gas interfaces, respectively. Typically for a PS film, the contact angle is between 8 and 12 degrees [1].

![Image](image.png)

**Figure 1.** Contact angle. The contact angle of the liquid droplet formed after the dewetting process is determined by Young’s equation. In the graph, $\gamma_{lg}$ represents the liquid-gas surface tension, $\gamma_{ls}$ represents the liquid-solid surface tension, and $\gamma_{sg}$ represents the solid-gas surface tension.

The dewetting process can be seen in figure 2. The images correspond to a dewetting process of a PS film. The figure is extracted from the work done by Reiter [1].

When the liquid used is homogeneous, the shape of the droplet is determined by the surface tensions according to Young’s equation. However, if the composition of the liquid is anisotropic, the shape of the droplet changes. The competition between the surface tensions and the internal structure determines the ultimate droplet shape. For example, by anisotropy effects, droplet formation with pyramidal structure has been observed in lamella phase copolymer systems [2].

Confining a copolymer alters its structure in volume. By using a dewetting process, nano-rings, obtained by confining a mixture of copolymers with a hexagonal structure in nano-droplets [3], have been manufactured.
Figure 2. Optical microscopy image. Dewetting process of a PS film, supported on a silicon substrate. 

a- Thermal instabilities propagate on the film surface causing it to break into small holes. b- The size of the holes increases with time. c- The collision of the holes causes boundaries formation. d- The advanced stage of dewetting ends with the destabilization of the boundaries forming small drops. The figure has been extracted from the work realized by Reiter [1].

2. Copolymer nano-droplet model

2.1. Copolymer-solvent System.

We can express the free energy of a ternary copolymer-solvent system as a function of the order parameters $\eta$ and $\phi$, where $\phi$ represents the composition of the copolymer mixture and $\eta$ represents the solvent [4,5].

Energy is composed of a short-range term $F_s[\phi, \eta]$ and a long-range term $F_l[\phi]$

The short-range term is:

$$ F_s[\phi, \eta] = \int d\mathbf{r} \left[ f_\eta(\eta) + f_\phi(\phi) + W(\phi, \eta) + \frac{D_1}{2} |\nabla \eta|^2 + \frac{D_2}{2} |\nabla \phi|^2 \right] $$

Where $D_1$ and $D_2$ are phenomenological parameters related to interface energy. The expressions $f_\eta(\eta), f_\phi(\phi)$ refer to double-well potentials, specifically:

$$ f_\eta(\eta) = -\frac{1}{2} c_1 \eta^2 + \frac{u_1}{4} \eta^4 $$

$$ f_\phi(\phi) = -\frac{1}{2} c_2 \phi^2 + \frac{u_2}{4} \eta \phi^4 $$

Where $c_i$ and $u_i$ are phenomenological constants.

The expression $W(\phi, \eta)$ indicates the potential of interaction between both order parameters. It is given by:

$$ W(\phi, \eta) = b_1 \phi \eta - \frac{b_2}{2} \eta \phi^2 + \frac{b_3}{2} \eta^2 \phi^2 - \frac{1}{2} b_3 \eta^2 \phi $$

The long-range term is:

$$ F_l[\phi] = \int d\mathbf{r} \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') (\phi(\mathbf{r}) - \bar{\phi}) (\phi(\mathbf{r}') - \bar{\phi}) $$
The expression above is related to the $\phi$ parameter that represents the copolymer. The interaction potential $b_i$ parameters characterize the interactions between copolymer blocks and the solvent. The evolution of order parameters $\phi$ and $\eta$ represents the evolution of the copolymer and the solvent, respectively. Time evolution results in a set of coupled differential equations for conserved order parameters

\[ \frac{\partial \eta}{\partial t} = \nabla^2 \left( \frac{\partial F}{\partial \eta} \right) \] (11)

\[ \frac{\partial \phi}{\partial t} = \nabla^2 \left( \frac{\partial F}{\partial \phi} \right) \] (12)

### 2.2. Simulation of the Copolymer-solvent System.

The Eyre algorithm previously developed [6] for a copolymer system can be adapted to solve the set of Cahn-Hilliard equations that model the time evolution of the copolymer and the solvent equations (11) and (12). The algorithm expression is:

\[ \phi_t + \Delta t \nabla^2 \left( - (1 - a_1)c_2 \phi_t + D_2 \nabla^2 \phi_t + \Delta t \alpha \phi_t + \Delta t \nabla^2 \left( - a_1 c_2 \phi_t^3 + b_1 \eta - b_2 \eta \phi - \frac{b_3}{2} \eta^2 + b_4 \eta^2 \phi \right) \right) \]

\[ \eta_t + \Delta t \nabla^2 \left( - (1 - a_2)c_1 \eta_t + D_1 \nabla^2 \eta_t + \Delta t \nabla^2 \left( - a_1 c_1 \eta_t^3 + b_1 \phi - \frac{b_3}{2} \eta^2 - b_3 \phi \eta + b_4 \eta \phi \right) \right) \]

With the following stability conditions

\[ a_1 \geq \frac{1}{c_2} \left[ \frac{c_2}{2} + \frac{3}{2} b_2 + 3u_2 \right] \] (15)

\[ a_2 \geq \frac{1}{c_1} \left[ \frac{c_1}{2} + \frac{3}{2} b_3 + 3u_1 \right] \] (16)

### 2.3. Simulation of Copolymer Nano-droplets on Rigid Substrate.

To simulate the temporal evolution of a copolymer droplet deposited on a rigid substrate, the air copolymer system was modeled as a ternary system (solvent copolymer), where the air was treated as a bad solvent. The interaction with the substrate was simulated through a potential of the form:

\[ P(x, y, z) = P_0 \exp \left[ - \frac{z}{z_0} \phi \right] \] (17)
Where the $P_0$ sign determines the preference towards one of the blocks of the copolymer. The $z_0$ term determines the extent of the interaction potential. The $z$ coordinate refers to the normal direction to the substrate. Figure 3 illustrates the represented system.

![Figure 3. Schematic representation of the simulated system. A droplet of copolymer on a rigid substrate.](image)

The system was simulated with a 128x128x64 ($x, y, z$) grid with $\Delta x = \Delta y = \Delta z = 0.3$ and $\Delta t = 2$. Periodic boundary conditions in the $x$ and $y$ direction and no flow in the $z$ direction were used. Eyre algorithm developed in section 2.2 was used for time evolution, and spatial derivatives were resolved using a spectral method.

### 3. Results and discussion

The effect of confinement for lamellae bulk structures, cylinders and BCC structures was studied.

- $c_1 = 0.1, u_2 = 1, D_2 = 1 \ y \alpha = 1, \phi = 0$ was used for the lamellae system.
- $c_1 = 0.1, u_2 = 1, D_2 = 1 \ y \alpha = 1, \phi = 0.05$ was used for the cylinder system.
- $c_1 = 0.1, u_2 = 1, D_2 = 1 \ y \alpha = 1, \phi = 0.1$ was used for the BCC system.

The interaction between the air and the copolymer was modeled by considering air as a bad solvent, i.e. with a low affinity between the solvent and the copolymer. For this purpose, the values of the interaction potential were chosen appropriately.

The interaction parameters $b_2 = 0.5, b_3 = 0$ and $b_4 = 1$ were chosen to obtain low affinity between the solvent (air) and the copolymer.

The interaction between the copolymer and the substrate was simulated by the external potential presented in equation 17. To study the effects of the substrate on the morphologies obtained, different values for the $P_0$ interaction were used. To the $z_0$ parameter was assigned a value of 0.1, which limits the interaction of the potential to an extremely small distance near the wall, much less than the radius of gyration of the molecules.

The initial condition is illustrated in Figure 4, and represents the conformation of a disorderly phase copolymer confined to a nano-droplet deposited on a substrate.
Figure 4. Initial conditions of order parameters $\phi$ and $\eta$ respectively. The initial condition represents a droplet of disorderly phase copolymer supported on a substrate.

The lamellar phase was simulated for different values of $b_1$ and $P_0$. The above parameters represent the affinity of one of the copolymer blocks with the air and the substrate. The relationship between the two generates different morphologies of the copolymer droplets.

Figure 5 illustrates the different structures developed by the copolymer confined in a nano-droplet. In all cases, the droplet has a pyramidal type shape, induced by the lamellar structure of the copolymer. A parallel orientation to the substrate is observed in all cases.

Experimental work in the literature shows a similar formation of structures within the nano-droplets. Figure 6, specially, shows the image of a nano-droplet obtained by the dewetting process of a diblock polystyrene-poly(methyl methacrylate) (PS-PMMA) copolymer in the lamellae phase. Details can be found in the work of Croll et al.[2].

Figure 5. Nano-droplet structures obtained for a bulk phase copolymer of lamellae. The images reflect the interaction of the substrate and the free surface, which determine the final shape of the nano-droplet. The values of the interaction are a- $P_0 = 0.01, b_1 = 0.03$, b- $P_0 = 0.01, b_1 = 0.03$ c- $P_0 = 0.01, b_1 = 0.05$ d- $P_0 = 0.02, b_1 = 0.02$. Figures c and d show a cut to observe inside the droplet.
Figure 6. AFM image. Nano-droplet of copolymer in lamellae phase obtained by the dewetting process. The image shows the stepwise shape of the droplet induced by the competition between the surface tension on the liquid surface and the lamellae structure forming the copolymer droplet. The image was extracted from the work of Croll et al. [2].

Note the excellent alignment between the results obtained from the simulation (figure 5 panel a), and the experimental data reported in the literature, shown in figure 6.

The BCC phase was simulated for different $b_1$ and $P_0 = 0.02$ values. In figure 7, the different obtained morphologies are illustrated.

In this case, the morphologies correspond to a fixed value of interaction with the substrate and different values of interaction with the air or the solvent. When the air interaction is smooth, the droplets morphology presents a great similarity with those obtained in spherical confinement for copolymers [7] in BCC phase (Figure 7, panels a and b). With strong air interaction, the BCC structure is strongly altered, forming a concentric lamellar structure (figure 7 panel c).

Figure 7. Nano-droplet structures obtained for a bulk phase copolymer of BCC spheres. The images reflect the interaction of the substrate and the free surface, which determine the final shape of the nano-droplet. The interaction values are a- $P_0 = 0.02, b_1 = 0.01$ b- $P_0 = 0.02, b_1 = 0.01$ c- $P_0 = 0.012, b_1 = 0.06$. Figure c is shown in cut to observe the inside structure.

The hexagonal phase was simulated for different $b_1$ and $P_0 = 0.02$ values.
The different structures developed by the copolymer confined in a nano-droplet are illustrated in figure 8 where the images correspond to increasing $b_1$ values. The strong confinement induced by the substrate and the air produces a marked alteration of the hexagonal phase. Due to bending effects, the cylinders are transformed into rings parallel to the substrate.

Experimental works present in literature show a similar formation of nano-rings obtained in droplets generated by dewetting [3]. Particularly, the image of a nano-droplet obtained by the PS-PS copolymer dewetting process in hexagonal phase of cylinders is presented in figure 9. Details are available in the work of Shaw et al. [3].

Note the excellent alignment between the experimental results present in the literature and the simulations performed.

**Figure 8.** Non-droplet structures obtained for a bulk phase copolymer of hexagonal arrangements. The images reflect the interaction of the substrate and the free surface, which determine the nano-droplet final shape. The interaction values are a- $P_0 = 0.02, b_1 = 0.01$ b- $P_0 = 0.02, b_1 = 0.02$ c- $P_0 = 0.02, b_1 = 0.03$ d- $P_0 = 0.02, b_1 = 0.04$.

**Figure 9.** TEM image. Nano-droplet of copolymer in phase of cylinders in hexagonal arrangements obtained by the dewetting process. The strong confinement transforms the copolymer bulk structure. The process allows to produce nano-rings. Experimental details are available in the work done by Shaw et al [3].
4. Conclusions
Bulk morphologies of diblock copolymers have been extensively studied in the literature both experimentally and theoretically. Depending on the composition of the blocks it is comprised of, the bulk structures correspond to lamellae, gyroids, cylinder hexagonal arrangements and BCC sphere structures.

Recent research has shown that confinement is a powerful tool to break the symmetry of a structure, and obtain new shapes, different from those of bulk.

The process of formation of new morphologies by confinement in nano-droplets, created from a dewetting process, was simulated. The obtained structures showed a great similarity with the experimental results present in the literature.

The developed model captures the fundamental interactions that determine the dynamics of the phase separation process of a copolymer system confined between a rigid substrate and a free surface. Furthermore, its numerical resolution is highly efficient as a result of the implementation of Eyre algorithm.

5. References
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