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HYDRODYNAMIC EFFECTS OVER THE SELF ASSEMBLY OF DIBLOCK COPOLYMER MELTS

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Abstract. *Diblock copolymers have been extensively used for fabricating functional materials due to their ability to spontaneously form ordered microscale structures. These microscale structures are formed under a certain temperature, where the copolymer molecules transition from a disordered to an ordered state. It is known that hydrodynamic effects strongly influence pattern formation, particularly in lamellar patterns. In this study, we investigate the impact of hydrodynamic effects on the self-organization of diblock copolymers. We compare our results with and without hydrodynamic effects after an initially disordered configuration reaches a stable configuration over time.*

Keywords: *Diblock copolymer, Functional material, Microscale structures, Hydrodynamics, Patterns.*

1. INTRODUCTION

Diblock copolymers are polymers composed of two types of monomers. A diblock copolymer melt is a diblock copolymer in the absence of a solvent. In this type of polymer molecule, the monomers are grouped together into two blocks, referred to as block A and B. These two blocks are connected to each other at one of their extremities by a covalent bond (see, for example, Choksi and Ren (2003)). Due to this connectivity, even if block A and B have mutually unfavorable solubility, macrophase separation cannot occur. The only way for these different blocks to segregate is within the molecule's own length scale, leading to microphase separation. This spontaneous organization of the diblock copolymer molecules, called self assembly, occurs after this type of material is quenched and undergoes a phase transition.

Due to the unfavorable solubility and the connectivity between blocks, this type of copolymer can self-organized in a variety of morphologies, some of which are of interest for fabricating functional materials. For instance, according to Thurn-Albrecht *et al.* (2000), diblock copolymers are used in the fabrication of a matrix for producing a high-density nanowires, pointing towards the possibility of creating a high-density storage media. Also, according to Wong *et al.* (2020), diblock copolymers can be used to fabricate nanoreactors and nanoporous microparticles with promising applications in biomedicine.

Therefore, over the past few decades, efforts have been made to develop a theory that describes microphase separation in order to precisely predict the pattern formation of diblock copolymers without the need for trial and error through experimentation. Thus, additional effects, which are already known to participate in the self organization needs to be considered in the theoretical description. For example, according to Bahiana and Oono (1990), the hydrodynamic effects are responsible to induce a well-ordered lamellar structures.

In this work, using a continuum description, similar to the study of Honda and Kawakatsu (2008), we investigate at what conditions the hydrodynamic effects are expected to be relevant over the equilibrium morphology for a symmetric diblock copolymer melt.

2. PROBLEM DEFINITION

The dimensionless free energy functional for a diblock copolymer melt in the context of mean-field theory, originally derived by Ohta and Kawasaki (1986), is given by

$$F\{\varphi\} = \int_{\Omega} f(\varphi)\, d\mathbf{x} + \frac{\lambda}{2}\int_{\Omega} |grad\,\varphi|^2\, d\mathbf{x} + \frac{\omega}{2}\int_{\Omega}\int_{\Omega} G(\mathbf{x},\mathbf{y})\,(\varphi(\mathbf{x}) - \overline{\varphi})\,(\varphi(\mathbf{y}) - \overline{\varphi})\; d\mathbf{x}\, d\mathbf{y}, \tag{1}$$

where $grad$ denotes the gradient, φ is the order parameter, λ and ω are positive dimensionless parameters, $f(\varphi)$ is a symmetric double-well potential with $f(\varphi) = 0$ at $\varphi = -1$ and $\varphi = 1$, and G is a Green function defined by

$$\Delta G(\mathbf{x},\mathbf{y}) = -\delta(\mathbf{x} - \mathbf{y}), \tag{2}$$

where Δ is the laplacian operator and δ the Dirac delta function.

From Eq. (1) and Eq. (2), is possible to derive an evolution equation for the order parameter φ, considering a diffusion driven by the gradient of the chemical potential as

$$\mathbf{j} = -M\nabla\mu, \tag{3}$$

where the chemical potential μ is defined as

$$\mu = \frac{\delta F\{\varphi\}}{\delta\varphi}, \tag{4}$$

being M a parameter which contains the diffusional Peclet number. Thus, the conservation law

$$\dot{\varphi} = -\nabla\cdot\mathbf{j}, \tag{5}$$

allows us to obtain the system of equations

$$\left.\begin{aligned}\dot{\varphi} &= M(\Delta\mu - \omega(\varphi - \overline{\varphi})),\\ \mu &= -\lambda\Delta\varphi + f'(\varphi),\end{aligned}\right\} \tag{6}$$

which describes the evolution of the order parameter φ, and where the boundary conditions used are generally periodicity or no-flux type boundary condition for φ and μ.

Although this description is able to predict many equilibrium morphologies known from experiments, it does not considers many other additional effects involved on the dynamics of the self assembly, as for instance, momentum effects. Thus, based on the work of Cheng *et al.* (2017), a more general description will be provided by the system of equations Eq. (7), where we add to the description a momentum balance equation and a incompressibility condition (Eq. (7c) and Eq. (7d)).

$$\left.\begin{aligned}\dot{\varphi} + \mathbf{u}\cdot grad\,\varphi = M(\Delta\mu - \omega(\varphi - \overline{\varphi})),\\ \mu = -\lambda\Delta\varphi + f'(\varphi),\\ \dot{\mathbf{u}} + (grad\,\mathbf{u})\,\mathbf{u} + grad\,p - \frac{1}{Re}\Delta\mathbf{u} + K\varphi\, grad\,\mu = 0,\\ div\,\mathbf{u} = 0,\end{aligned}\right\} \tag{7}$$

where $\mathbf{u}$ is the dimensionless velocity, p is the dimensionless pressure, K is a dimensionless parameter which contains the Webber number and Re is the Reynolds number. The boundary conditions used, according to Cheng *et al.* (2017) are either periodicity or no-flux type boundary condition for φ, μ and $\mathbf{u}$.

3. NUMERICAL DETAILS

We have used the finite element software COMSOL Multiphysics to simulate the spontaneous ordering and find the equilibrium morphology of the diblock copolyer melt in a square domain. The system of equations Eq. (6) and Eq. (7) with periodic boundary conditions for the variables φ, μ and $\mathbf{u}$ were implemented in the COMSOL Multiphysics using the weak form in Mathematics Module. We have discretized a 1 by 1 dimensionless domain with square elements using a second order Lagrange shape function for all variables with exception for the pressure, which we used a linear shape function. We adopt a regular grid with 100 by 100 elements. For the time discretization, we apply an implicit second-order BDF method. At each time-step, the discrete mixed problem results in a system of nonlinear equations that is solved through a fully coupled approach using the damped Newton method. The direct solver PARDISO was selected to solve the discrete system.

4. RESULTS

In this section we show some numerical results for the equilibrium morphology for a diblock copolymer melt using

$$M = 1,\ K = 1,\ \lambda = 7\times10^{-5},\ \omega = 5\times10^{2}. \tag{8}$$

As initial condition, we assume

$$\varphi(t=0) = \overline{\varphi} + 0.01\,rand(x,y), \tag{9}$$

which represents a small perturbation in the concentration field around a uniformly mixed state given by $\overline{\varphi}$, and where $rand$ is a random function which can have any value from -1 to 1. This initial condition for φ is shown in Fig. 1.

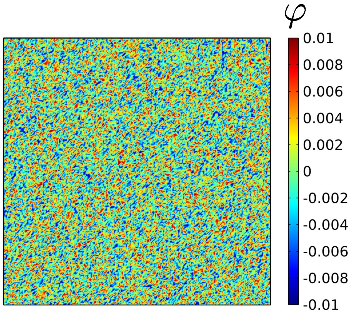

Figure 1. Initial random distribution for $\varphi(t = 0)$ with $\overline{\varphi} = 0$.

For this study, we set $\overline{\varphi}$ fixed in 0, which represents a symmetric diblock copolymer, and choose conveniently as the double-well potential $f(\varphi) = \frac{1}{4}(\varphi^2 - 1)^2$. For the initial velocity and pressure, we set $\mathbf{u} = 0$ and $p = 0$. Thus, the flow develops purely by the gradient of the chemical potential. Following the work of Cheng *et al.* (2017), we consider a periodic boundary condition for φ, μ and $\mathbf{u}$. Considering the two different system of equations given by Eq. (6) and Eq. (7), we have computed the φ distribution at $t = 40000$. Our results, shown in Fig. 2, demonstrate that the increase of the Reynolds number induces ordering for the lamellar pattern. This resultrs are in agreement with the work of Bahiana and Oono (1990), where is shown that, for the lamellar pattern formation, the inclusion of hydrodynamic effects produces well-ordered lamellae.

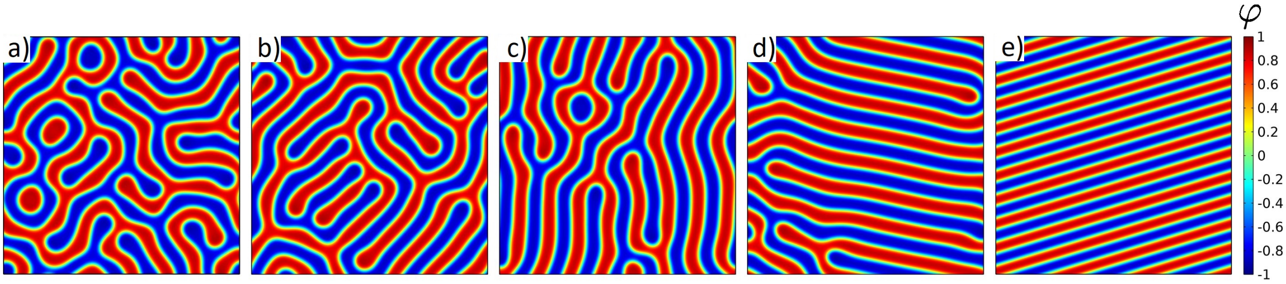

Figure 2. Order parameter φ distribution at $t = 40000$ for (a) considering only diffusion (Eq. (6)) and considering additional hydrodynamic effects (Eq. (7)) with (b) $Re = 1.4$, (c) $Re = 2$, (d) $Re = 5$ and (e) $Re = 8$.

5. CONCLUSIONS

In this work, we compared the description of microphase separation for a diblock copolymer melt, considering the addition of hydrodynamic effects, i.e., incorporating momentum into the dynamics of self-assembly. We demonstrated that pattern formation can change significantly depending on the magnitude of the Reynolds number. Our results also align with the existing literature on this problem.

6. REFERENCES

Bahiana, M. and Oono, Y., 1990. "Cell dynamical system approach to block copolymers". *Physical Review A*, Vol. 41, No. 12, p. 6763.

Cheng, Q., Yang, X. and Shen, J., 2017. "Efficient and accurate numerical schemes for a hydro-dynamically coupled phase field diblock copolymer model". *Journal of Computational Physics*, Vol. 341, pp. 44–60.

Choksi, R. and Ren, X., 2003. "On the derivation of a density functional theory for microphase separation of diblock copolymers". *Journal of Statistical Physics*, Vol. 113, pp. 151–176.

Honda, T. and Kawakatsu, T., 2008. "Hydrodynamic effects on the disorder-to-order transitions of diblock copolymer melts". *The Journal of chemical physics*, Vol. 129, No. 11.

Ohta, T. and Kawasaki, K., 1986. "Equilibrium morphology of block copolymer melts". *Macromolecules*, Vol. 19, No. 10, pp. 2621–2632.

Thurn-Albrecht, T., Schotter, J., Kastle, G.A., Emley, N., Shibauchi, T., Krusin-Elbaum, L., Guarini, K., Black, C., Tuominen, M. and Russell, T., 2000. "Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates". *Science*, Vol. 290, No. 5499, pp. 2126–2129.

Wong, C.K., Qiang, X., Müller, A.H. and Gröschel, A.H., 2020. "Self-assembly of block copolymers into internally ordered microparticles". *Progress in Polymer Science*, Vol. 102, p. 101211.

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