

Block copolymer lamellar thickness; an exactly solvable model

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 5297

(<http://iopscience.iop.org/0953-8984/1/31/029>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:34

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Block copolymer lamellar thickness; an exactly solvable model

Y Oono and M Bahiana

Department of Physics, Materials Research Laboratory and the Beckman Institute, 1110 W. Green Street, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Received 24 May 1989

Abstract. An exactly solvable model for the strongly segregated diblock copolymer melt is proposed, which gives an analytic expression for the concentration profile. The lamellar thickness L for the ordered phase as a function of the molecular weight M is analytically demonstrated to be $L \sim M^{2/3}$.

Diblock copolymers are polymers made by grafting two chemically distinct subchains A and B. In this Letter we consider only those diblock copolymers with equal length subchains. At lower temperatures these subchains tend to demix to form a lamellar phase (striped phase consisting of layers of codimension 1). Experimentally, it is possible to determine that $L \sim M^\alpha$, where M is the molecular weight. The value of α depends on the segregation regime: in the weak limit $\alpha = \frac{1}{2}$, and in the strong limit $\alpha = \frac{2}{3}$ (Hashimoto *et al* 1980). The purpose of the present Letter is to give an exactly solvable model of block copolymer morphogenesis in the strong segregation regime.

Helfand and Wasserman (1976) used a detailed chain picture to compute numerically the exponent $\alpha \approx 0.636$. Leibler (1980) derived the following Hamiltonian for the order parameter ψ of the block copolymer melt, where ψ is the monomer concentration difference of A and B species:

$$\mathcal{H} = \int d\mathbf{x} \frac{1}{2} \left[\left(\frac{\partial \psi}{\partial \mathbf{x}} \right)^2 + \Phi(\psi) \right] - \frac{1}{2M^2} \int d\mathbf{x} \int d\mathbf{y} G(\mathbf{x} - \mathbf{y}) \psi(\mathbf{x}) \psi(\mathbf{y}) \quad (1)$$

where $\Phi(\psi)$ is the local free energy function for which Leibler adopted the usual φ^4 functional form, and G is the Green function for the Laplacian under a suitable boundary condition. Here, unnecessary numerical constants have been suppressed. Using this Hamiltonian, Leibler (1980) could explain the weak segregation exponent. Ohta and Kawasaki (1986) derived the Hamiltonian more systematically, and variationally obtained $\alpha = \frac{2}{3}$ for the strong-segregation regime with the aid of an appropriate trial function. From a very different point of view, Oono and Shiwa (1987) arrived at the same system. They pursued a computationally efficient model which can exhibit striped patterns, and arrived at the following mathematical model:

$$\partial \psi / \partial t = \Delta(\partial \Phi / \partial \psi - \Delta \psi) - b \psi \quad (2)$$

where b is a phenomenological positive parameter. When $b = 0$, this equation reduces to the Cahn–Hilliard equation. The model turns out to be a time-dependent Ginzburg–

Landau equation for the conserved order parameter with the Leibler (1980) Hamiltonian (1). The relation between b and the molecular weight M was fixed as $b \propto 1/M^2$ through (i) a dimensional analytical argument, (ii) a numerical study of the equation and (iii) comparison of equations (1) and (2) (Oono and Bahiana 1988). In the same paper, the relation between the exponent α and the growth exponent for the spinodal decomposition was also pointed out. Recently Liu and Goldenfeld (1989) analysed the equation numerically, determined the density profile as well as the crossover behaviour between the weak- and strong-segregation limits and obtained $\alpha \approx 0.650$.

We have been making extensive use of the cell-dynamical system (CDS) models for spinodal decomposition and phase ordering of block-copolymer systems (actually the original model (Oono and Shiwa 1987) was a CDS version) to understand various features of phase ordering kinetics (Oono and Puri 1987, 1988). One of the fundamental problems is to find the minimal mathematical ingredients necessary to get the actually observed universal features. We have demonstrated numerically that the actual functional detail of Φ is not important in spinodal decomposition (Oono and Puri 1988); what is relevant is that Φ has two minima symmetrically placed around the local maximum at the origin, and the function grows sufficiently fast to infinity when $|\psi|$ becomes large. The detail of Φ affects only the interfacial structural detail and, in the case of spinodal decomposition, early time stages. A similar phenomenon can be demonstrated in the case of the block copolymers as well. In order words, if the function Φ satisfies the above mentioned abstract conditions, then the model with that Φ is in the same universality class of the ordinary spinodal decomposition in case $b = 0$ and in the same universality class of the ordinary block copolymers in case $b > 0$.

We shall exploit this universality or insensitivity to devise an analytically convenient model of the block copolymer system. Thus we use the following local free energy function:

$$\Phi(\psi) = \frac{1}{2}[\psi - \text{sgn}(\psi)]^2. \quad (3)$$

The function satisfies all the conditions mentioned above. To understand the equilibrium pattern we have to find the stationary solution to equation (2). With the free energy defined above, this corresponds to solving the linear ordinary equation for the codimension 1 lamellar pattern

$$d^2\psi/dx^2 - d^4\psi/dx^4 = b\psi. \quad (4)$$

Nonlinearity comes only through the matching condition between the domains with $\psi > 0$ and $\psi < 0$, which is dictated by the requirement for the continuity of the driving force $\psi - \text{sgn}(\psi) - d^2\psi/dx^2$ when $\psi = 0$. We look for an even periodic continuous solution with period $2L$ that is positive near the origin. A simple computation gives the following general form for the solution in $[-L/2, L/2]$:

$$\psi(x) = [1/\sqrt{(1-4b)}][(\cosh \beta x / \cosh(\beta L/2)) - (\cosh \alpha x / \cosh(\alpha L/2))] \quad (5)$$

where $\alpha = \sqrt{[1 + \sqrt{(1-4b)}/2]}$ and $\beta = \sqrt{[1 - \sqrt{(1-4b)}/2]}$. Thus for a given b ($< \frac{1}{4}$) there is a family of solutions with different periods $2L$. Notice that for sufficiently large L the obtained profile has extremal points near interfaces as was shown in the numerical solutions of Liu and Goldenfeld (1989).

The selection of the actually observable period is given by the minimum of the free energy density $F(L)$ of the system. In the strong-segregation limit the free energy density can be expanded in b as (unimportant constants are discarded)

$$\begin{aligned}\sqrt{(1-4b)}F(L) = & (1/L) \tanh(L/2) - 2\sqrt{b}(1/L) \tanh(L/2) \\ & + b(L^2/24 - 2/\cosh^2(L/2) - (1/L)19 \tanh(L/2) \\ & - (\tanh^2(L/2))/2 + \dots).\end{aligned}$$

We may discard transcendentally small terms, so that in the strong segregation limit, $1/\cosh(L/2)$ may be ignored, and $\tanh(L/2)$ may be set to unity. Thus minimisation of the above expansion (it is easy to demonstrate that the free energy is holomorphic in \sqrt{b} near the origin), we get the following asymptotic formula for L :

$$L = 2(2b/3)^{-1/3}(1 - 2\sqrt{b}/3 + \dots). \quad (7)$$

That is, $\alpha = \frac{2}{3}$. If we analyse the free energy formula above, it becomes clear that the dimensional analytic argument is actually exact. Thus the dimensional analytic derivation of this asymptotic exponent (Oono and Bahiana 1988) is not fortuitous.

The present model is not a good model for weak segregation regime, because the potential (local free energy) has a cusp at the origin. However, we can study the $L \rightarrow 0$ limit. The analytic formula for the free energy shows that if $b > 0.075\,235\dots$, $L = 0$, that is, the flat (disordered) phase is the state selected by the free energy minimum. The asymptotic power law $L \sim b^{-1/3}$ holds for $b < 0.01$. For larger b the effective exponent is smaller than $-\frac{1}{3}$. Thus our model does not give the so-called weak segregation regime power law $L \sim b^{-1/4}$. The derivation of this exponent usually relies on the observation that there is only one length scale in the problem. The present solvable model demonstrates that the argument is insufficient, since even in our model there is only one length scale in the weak segregation regime. For $\alpha = \frac{1}{2}$ it is crucial that the square gradient term in the free energy density dominates the contribution of the term Φ . This is possible only when the contribution from Φ is negligible at least qualitatively. For this to be true Φ must have a differentiable maximum near the origin. In our case Φ is of order ψ near the origin, so that, for smaller amplitudes of ψ , Φ dominates the free energy density, and the weak segregation exponent for our model becomes larger than $\frac{1}{2}$. More details will be discussed in our full paper about the CDS modelling of block copolymers.

The authors are grateful to Fong Liu and Nigel Goldenfeld for useful conversations and for their interest in this work. This work is, in part, supported by the National Science Foundation grant DMR 87-01393 and DMR 86-12860 (the latter through the Materials Research Laboratory of University of Illinois), and by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Brazil).

References

- Hashimoto T, Shibayama M and Kawai H 1980 *Macromolecules* **13** 1237
- Helfand E and Wasserman Z R 1976 *Macromolecules* **9** 879
- Leibler L 1980 *Macromolecules* **13** 1602
- Liu F and Goldenfeld N 1989 University of Illinois preprint
- Ohta T and Kawasaki K 1986 *Macromolecules* **19** 2621
- Oono Y and Bahiana M 1988 *Phys. Rev. Lett.* **61** 1109
- Oono Y and Puri S 1987 *Phys. Rev. Lett.* **58** 836
- Oono Y and Puri S 1988 *Phys. Rev. A* **38** 434
- Oono Y and Shiwa Y 1987 *Mod. Phys. Lett. B* **1** 49