

Lateral copolymer domain patterning through thermal gradients

Galen T. Pickett

Department of Physics and Astronomy, California State University, Long Beach, Long Beach, California 90840

(Received 22 October 2001; accepted 20 December 2001)

Lateral patterns in thin films of microsegregated copolymers can be controlled through the application of a static thermal gradient. Patterns are promoted lateral to the imposed gradient. Calculations in a lattice self-consistent field method are presented and compare favorably with predictions of a simple scaling theory. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1450546]

Control of self-assembled patterns is an increasingly important technological goal,^{1,2} and a proven equilibrium pattern-forming class of materials are the diblock copolymers,³ composed of a long run *A* monomers followed by another long run of a different monomer type, say *B*. At low temperature/high molecular weight, diblocks microsegregate producing a phase with a geometry and length scale dependent temperature and the composition of the chain. I will focus here on the lamellar phase, dominant for symmetric diblocks (equal amounts of *A* and *B* on the chain), as in Fig. 1. Long, parallel layers of *A*-rich material alternate with layers of *B*-rich materials, and the diblocks themselves stretch normal to the composition pattern.

In thin films this lamellar pattern occurs in one of two orientations.^{4–9} The stripes can lay in the plane of the substrate, or they can “stand up” so that the film overall presents a lateral pattern useful as templates. The equilibrium layer orients so as to lower the free-energy per chain. Even more interesting, perhaps, are driven, nonequilibrium methods for controlling the system. In this communication I consider static thermal gradients as a means to control lamellar orientation. Beyond strict thermal equilibrium, the first step is determining the steady-state driven structures that can appear when the temperature varies in space, but not in time.

Gradients in temperature can be imposed normal to a thin film by maintaining the substrate at an elevated temperature, while the free surface of the film held at a lower temperature. Heat will of necessity flow from the hot toward the cold surface, and the temperature profile will be linear, the appropriate solution to the static heat equation. Thermal gradients lateral to the substrate can be generated by locally heating the substrate, say through maintaining optical interference fringes in a static pattern.¹⁰

To get a handle on the ordering possibilities of fixed thermal gradients, it is useful to consider the simplest possible theory, one intended only to capture broad trends and the manner in which various quantities scale with molecular weight and film thickness. Initially, consider a microsegregated diblock film with a uniform thermal distribution. Further, as in Fig. 1, let us suppose that a single *A–B* domain is parallel to the film, of thickness *h*. A simple estimate of the free energy per chain here has been given by Alexander and deGennes.^{11,12} These (symmetric) diblocks have a total mo-

lecular weight *N*, the layer is completely filled with monomers, each occupying a volume a^3 where *a* is the typical monomer size. All geometric constants of order unity are suppressed, here. The number of chains per unit area, σ satisfies $\sigma = h/(Na^3)$. The thermodynamically incompatible *A* and *B* fluids come into contact at the height $z = h/2$, where *A* and *B* contacts raise the system free energy by a quantity proportional to the total area of contact between the *A* and *B* domains. On a per-chain basis, the amount of *A–B* contact area is simply $1/\sigma$, so that the thermal energy per chain is

$$F_{\text{thermal}} = \frac{\gamma}{\sigma} = \frac{\gamma N a^3}{h}, \quad (1)$$

where γ is the interfacial tension between *A*-rich and *B*-rich domains. In general γ is temperature dependent.

The entropic part of the free energy arises mainly (when $h \gg R_g$ the melt chain radius of gyration, $R_g \sim aN^{1/2}$) from stretching the diblocks over a distance *h*: The chain acts like a spring with a spring constant proportional to the inverse R_g squared:¹³

$$F_{\text{entropic}} = \frac{1}{2} \frac{h^2}{a^2 N}. \quad (2)$$

The overall chain free energy is thus

$$F_{\text{tot}}(h) = F_{\text{thermal}} + F_{\text{entropic}} = \frac{1}{2} \frac{h^2}{a^2 N} + \frac{\gamma N a^3}{h}. \quad (3)$$

The thickness of the layer is fixed, that is, not allowed to come to equilibrium, although *h* could certainly be chosen to match a convenient, known experimental length. The natural length scale is, of course, h_{eq} , the bulk repeat spacing of the lamellae in the bulk, which satisfies

$$\frac{dF_{\text{tot}}}{dh} = 0 \rightarrow h_{\text{eq}} = a^{5/3} \gamma^{1/3} N^{2/3}. \quad (4)$$

Without considering the details of exactly how the perpendicularly oriented domains encounter the neutral wall (an entropic interaction partially compatibilizes the *A* and *B* domains as they near the substrate^{6–9}) the perpendicular orientational energy is simply $F_{\text{tot}}(h_{\text{eq}})$. The perpendicularly oriented domains are free to space themselves in order to

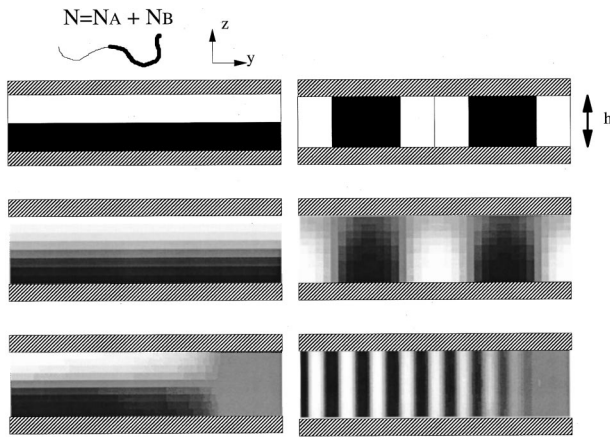


FIG. 1. Schematic: Here, a typical AB diblock is shown, with the typical orientations for the microsegregated lamellae. On the left are the parallel orientations. The upper figure is a schematic showing a single half-lamellar layer. The middle and lower figures show the output of the numerical SCF lattice calculations. In the middle-left, the thermal gradient is normal to the substrate, and at the bottom, the gradient is lateral to the substrate. The right column shows the situation for the perpendicular orientations. Note that near the “hot” end of the system, the diblocks are unsegregated. The lattice dimensions for the middle panels are $L_y=40, L_z=10$. The lower figures are substantially expanded in $y: L_y=200, L_z=10$.

minimize F_{tot} , while the parallel domains cannot. Thus, the difference in energy between the perpendicular and parallel orientations of the lamellar domains is

$$\Delta = F_{\text{tot}}(h) - F_{\text{tot}}(h_{\text{eq}}) = F_{\text{tot}}(h_{\text{eq}}) \left(\frac{x^2}{3} + \frac{2}{3x} - 1 \right), \quad (5)$$

where $x = h/h_{\text{eq}}$. Thus, for neutral substrates (A and B materials have the same surface energy), when the film thickness exactly matches the bulk equilibrium length scale ($x = 1$) the parallel and perpendicular orientations have the same energy,¹⁴ and, the perpendicular orientation is stabilized when $x \neq 1$. The incommensurability of film thickness and bulk repeat spacing has been proposed⁴ and observed experimentally⁵ to promote film lateral ordering.

Let us suppose, however, that the temperature field is not uniform in space, and furthermore that the AB interfacial tension γ is temperature-dependent (apart from the trivial scaling of all energies with kT implicit here). As long as there is no mass transport caused by the varying $\gamma(T(\vec{r}))$, the expressions above are still a valid estimate of a “free energy” which when minimized indicates the spontaneously occurring steady state.

Now, let $T = T(y)$, so that the temperature is a lateral function of position, as in Fig. 1, lower left. For a parallel oriented film, established in this nonuniform $T(y)$:

$$F_{\text{tot}} = \frac{h^2}{2a^2 N} + \frac{\int_0^{L_y} dy \gamma(y) N a^3 h^{-1}}{\int_0^{L_y} dy} \rightarrow F_{\text{tot}}^{\parallel} = \frac{h^2}{2a^2 N} + \frac{N a^3}{h} \langle \gamma \rangle, \quad (6)$$

where $\langle \gamma \rangle$ is the spatial average of $\gamma(\vec{r})$. If further, h is chosen to minimize $F_{\text{tot}}^{\parallel}$, then

$$F_{\text{tot}}^{\parallel} = \frac{3}{2^{2/3}} a^{4/3} N^{1/3} \langle \gamma \rangle^{2/3}. \quad (7)$$

The parallel oriented film with lateral gradients in γ has the same free energy as an unstrained lamellar layer held at the average temperature of the system.

In the perpendicular orientation, the calculation is a bit more complicated. Here, we have a collection of separate lamellar domains, each one characterized by a different $\gamma(y)$. Roughly speaking a stripe with its AB interface located at y will have an overall equilibrium size set by the local value of $\gamma(y)$. Thus, the free energy per chain can be calculated as

$$F_{\text{tot}}^{\perp} = \frac{\int_0^{L_y} dy \frac{3}{2^{2/3}} a^{4/3} N^{1/3} \gamma(y)^{2/3}}{\int_0^{L_y} dy} = \frac{3}{2^{2/3}} a^{4/3} N^{1/3} \langle \gamma^{2/3} \rangle. \quad (8)$$

Thus, in the presence of an inhomogeneous $\gamma(y)$, the quantity controlling the ordering of the lamellar domains is (in the most possibly favorable parallel scenario, when $h = h_{\text{eq}}$ for the half-layer)

$$\Delta = F_{\text{tot}}^{\parallel} \left[1 - \frac{\langle \gamma^{2/3} \rangle}{\langle \gamma \rangle^{2/3}} \right]. \quad (9)$$

As a result of the concavity of the function $x^{2/3}$, Δ is negative definite, thus stabilizing the perpendicular domains. Roughly speaking, the entire parallel layer is either compressed too much, or stretched out too much. The perpendicular layer allows the stretching energy in the various stripes to adjust itself to be in equilibrium with the local AB surface tension.

Clearly, if the layer thickness is many many equilibrium repeat spacings, and if $\gamma = \gamma(z)$, the situation will be exactly the same. That is, with the thermal gradients in the normal direction, lateral patterns are suppressed. However, with a single AB layer in the system, there is a different free energy comparison. Here, there is effectively a single γ in the system, $\gamma(h/2)$, since that is the location of the one and only interface. Now the stability of the competing orientations can be tuned through controlling $\gamma(h/2)$ on the one hand and $\langle \gamma^{2/3} \rangle$ on the other. When the thermal profile is linear, so that $\gamma(z) = \gamma_o(1 + \alpha z/h)$, parallel orientations can be favored depending on the precise value of h . So, the general conclusion from the scaling theory is that the two moments, $\langle \gamma \rangle$, and $\langle \gamma^{2/3} \rangle$, of the surface tension serve to determine the stability of the orientations.

To check these ideas, I performed lattice self consistent field (SCF) calculations. This method is a mature numerical technique.¹⁵ The details of the implementation of this method are set out in many places, and for brevity’s sake I only mention here what has to change to model thermal gradients. While there is a great freedom available in designing, and controlling the thermal profile of the layer, I start here with the simplest possible. I consider two scenarios, namely gradients normal to the substrate, and gradients perpendicular to the substrate. For the normal case,

$$\chi_{AB}(\vec{r}) = \chi_{\text{bot}} - (\chi_{\text{top}} - \chi_{\text{bot}}) \frac{z}{L_z}, \quad (10)$$

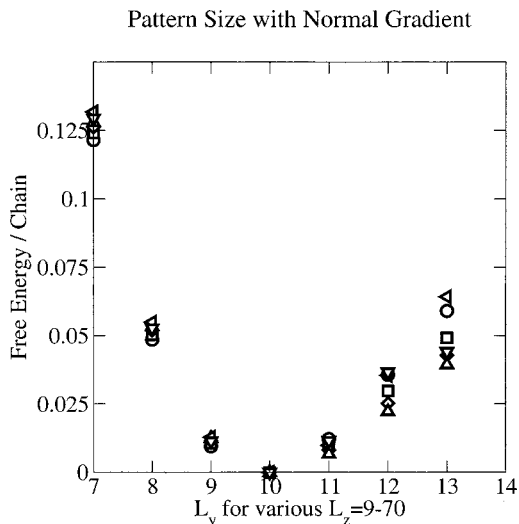


FIG. 2. Lateral Dimension: With a normal thermal gradient of magnitude $\epsilon = 1.0$, here is shown the free energy per chain for several film thicknesses when the lateral dimension of the repeating pattern is varied from $L_y = 7-13$. For each value of film thickness, the lateral dimension which minimizes the free energy per chain is $L_y = 10$ —the same length scale for diblock in the bulk with the average value of $\chi = 0.1$.

while in the lateral case, I have chosen

$$\chi_{AB}(\vec{r}) = \chi_{\text{left}} - (\chi_{\text{right}} - \chi_{\text{left}}) \frac{y}{L_y}, \quad (11)$$

where $\chi_{AB}(\vec{r})$ is the spatially varying Flory–Huggins interaction parameter between A and B monomers. The $L_z \times L_y$ calculation lattice has impenetrable, neutral surfaces at $z = 1$ and $z = L_z$, and the vertical surfaces $y = 1$ and $y = L_y$ are maintained as planes of reflection symmetry in the infinite layer. Thus, the lateral gradients are actually a sawtooth pattern in an infinite film. Surprisingly little has to change in the lattice model. For example, A -monomer potential is

$$U_A(\vec{r}) = \alpha(\vec{r}) + \chi_{AB}(\vec{r}) \langle \phi_B \rangle. \quad (12)$$

In this expression, $\alpha(\vec{r})$ is the hard-core incompressibility potential, and $\langle \rangle$ refers to the usual lattice contact fraction.

When the gradient in χ_{AB} is normal to the plane of the film, the prediction of the simple Alexander theory is that the repeat spacing of the microsegregated lamellae is the same as the bulk spacing for the average value of χ_{AB} in the system, occurring when a single $A-B$ layer occupies $z = 1 - L_z$, as in Fig. 2. Here, I have plotted the free energy per chain as a function of the (as yet unknown) layer spacing, L_z . In equilibrium, L_z would be chosen to minimize this free energy. As in Fig. 2, this is accomplished uniformly when L_z is maintained at its value appropriate to $\langle \chi_{AB}(\vec{r}) \rangle$. In this example, $N_A = 75 = N_B$, $\chi_{\text{top}} = 0.5$ and $\chi_{\text{bot}} = 0.15$. Thus, the spatial average of χ is $\langle \chi_{AB} \rangle = 0.1$. For each value of $L_z = 9-70$, I varied $L_y = 7-13$ and verified that in each instance $L_y = 10$ minimized the perpendicular pattern energy. This corresponds well with the bulk spacing for diblocks at the average $\chi = 0.1$ of 10 lattice units.

It is interesting that this prediction of the Alexander model survives in the present case. It is known that the order-disorder transition for symmetric diblocks occurs for

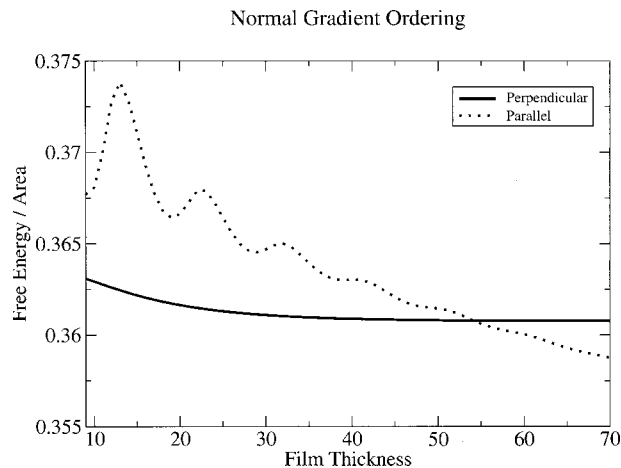


FIG. 3. Normal gradient: Here, the free energy per surface area for perpendicular and parallel oriented domains is shown. Clearly, for these normal thermal gradients, the parallel orientation is progressively stabilized at fixed ϵ as the film thickness is increased.

$\chi_{AB} N_{\text{tot}} \approx 10.5$. Near the lower substrate, $\chi_{AB} N \approx 0.15 \times 150 = 22.5$, well above the ODO transition. Near the upper substrate, however, $\chi_{AB} N_{\text{tot}} \approx 7.5$. Indeed, the local profiles indicate that in both the perpendicular as well as the parallel orientations, the diblock fluid near the “warm” surface is not microsegregated, but that the segregation occurs in the layer, and becomes stronger as the colder surface is approached. This is clearly visible in Fig. 1. Near the “hot” edge of the lattice, the diblocks are unsegregated, and become progressively more strongly segregated as the “cold” surface is approached.

As in Fig. 3, when the thermal gradient is linear and normal to the substrate, the parallel orientation is progressively stabilized. Here, the free energy per unit area for each orientation is shown. The degree of stability depends on the film thickness, and contrary to the Alexander consideration, the perpendicular orientation has a “head start” in terms of stability that eventually is overcome with increasing film thickness, and therefore a smaller and smaller penalty to realize the parallel orientation.¹⁴ The oscillations in the parallel orientation (dashed line) are caused by the appearance of successive half-lamellar layers. The perpendicular orientation does not display these oscillations, for as the layer is made thicker, one is merely adding more material to the center of the film (in other words, adding material at the position corresponding to the average value of χ_{AB}), and hence approaches a constant value for large thicknesses. In short, normal gradients tend to stabilize the film-parallel orientations.

On the other hand, gradients lateral to the film direction stabilize the perpendicular orientation for the lamellar pattern, as in Fig. 4. Here, the lattice is fixed at $L_y = 200$ and $L_z = 10$, while the amplitude of the thermal gradient is increased. Here,

$$\epsilon \equiv \frac{\chi_{\text{bot}} - \chi_{\text{top}}}{\langle \chi_{AB} \rangle} \quad (13)$$

where the average value of χ_{AB} is held fixed by $\langle \chi_{AB} \rangle = 0.1$, again for symmetric diblocks of total molecular weight $N = 150$. Here, the perpendicular orientation is clearly

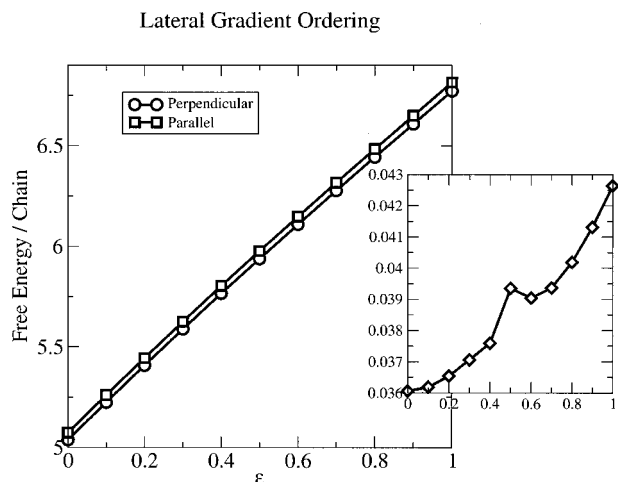


FIG. 4. Lateral gradient: Here, the free energy per chain in each of the perpendicular and parallel oriented films is shown for fixed film thickness and lateral dimension ($L_y=200$, $L_z=10$). The perpendicular film is stabilized more and more as the magnitude of the gradient is increased (by an amount shown in the inset). Lateral gradients promote, in this case enhance, perpendicular ordering.

stable across the entire range of ϵ , and as the inset diagram shows, the degree of the stabilization increases as the gradient is increased in magnitude. Here, the oscillation in the difference free energy (inset curve) shows characteristic oscillations as lamellar layers are melted near the high-temperature areas.

Alexander-model and SCF calculations yield the same conclusion. Control over the direction of static thermal gra-

dients is tantamount to microscopic control of lamellar orientation. This conclusion will be drastically altered, of course, if a hydrodynamic instability (surface-tension induced convection, say) occurs in the system, a highly interesting scenario for future study.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for support of this research.

- ¹R. D. Peters, X. M. Yang, Q. Wang, J. J. de Pablo, and P. F. Nealey, *J. Vac. Sci. Technol. B* **18**, 3530 (2000).
- ²L. Yan, W. T. S. Huck, X.-M. Zhao, and G. M. Whitesides, *Langmuir* **15**, 1208 (1999).
- ³M. W. Matsen and F. S. Bates, *Macromolecules* **29**, 1091 (1996).
- ⁴D. G. Walton, G. J. Kellogg, A. M. Mayes, P. Lambooy, and T. P. Russell, *Macromolecules* **27**, 6225 (1994).
- ⁵G. J. Kellogg, D. G. Walton, A. M. Mayes, P. Lambooy, T. P. Russell, P. D. Gallagher, and S. K. Satija, *Phys. Rev. Lett.* **76**, 2503 (1996).
- ⁶G. T. Pickett, T. A. Witten, and S. R. Nagel, *Macromolecules* **26**, 3194 (1993).
- ⁷Galen T. Pickett and Anna C. Balazs, *Macromolecules* **30**, 3097 (1997).
- ⁸M. W. Matsen, *J. Chem. Phys.* **106**, 7781 (1997).
- ⁹W. H. Tang, *Macromolecules* **33**, 1370 (2000).
- ¹⁰X. M. Yang, R. D. Peters, P. F. Nealey, H. H. Solak, and F. Cerrina, *Macromolecules* **33**, 9575 (2000).
- ¹¹S. A. Alexander, *J. Phys. (Paris)* **38**, 983 (1977).
- ¹²P.-G. de Gennes, *J. Phys. (Paris)* **37**, 1443 (1976).
- ¹³P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- ¹⁴There is always a small interaction, not included in this simple theory that stabilized the perpendicular domains, as described in Refs. 6–9. This stabilization is evident in the SCF calculations, Fig. 4 especially.
- ¹⁵G. Fleer, M. A. Cohen-Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Chapman and Hall, London, 1993).