

Comment on “Cylindrical phase of block copolymers: Stability of circular configuration to elliptical distortions and thin film morphologies”

M. W. Matsen

Polymer Science Centre, University of Reading, Whiteknights, Reading RG6 6AF, United Kingdom

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Pereira [Phys. Rev. E **63**, 061809 (2001)] has recently predicted that the hexagonal symmetry of the cylindrical phase in *AB* diblock copolymer melts is highly unstable. This is in stark disagreement with experiment, and can be attributed to the fact that the connectivity of the *A* and *B* blocks is not enforced in his implementation of the strong-segregation theory. Here, the stability of the hexagonal symmetry is supported by alternative calculations based on a more advanced strong-segregation theory that enforces the connectivity as well as the more rigorous self-consistent field theory.

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Pereira [1] has recently examined the cylindrical phase of a diblock copolymer melt using strong-segregation theory (SST) [2], and found that a hexagonal unit cell is unstable with respect to a deformation. In fact, he predicts that the unit cell deforms to aspect ratios of up to $\Lambda \approx 1.4$ (see Fig. 1) [3]. This result is highly unexpected and contradicts our present understanding that the entropic stretching energy favors domains of uniform thickness [4,5]. If we accept this prediction, we should also expect other structures, such as the spherical phase, to be affected in a similar way.

To our knowledge, such a deformation has never been suggested by experiment despite numerous transmission electron microscopy studies. In shear-oriented samples where the microtomed slice is known to be perpendicular to the cylindrical axis [6], any distortion $\geq 20\%$ from hexagonal symmetry should be readily observed. Small-angle scattering studies provide even further compelling evidence. Powder patterns from unoriented samples of the cylinder phase display a sequence of peaks at the relative positions, $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\dots$, characteristic of hexagonal symmetry [7]. Here, any distortion $\geq 10\%$ would produce an obvious splitting of the peaks. Additional support for hexagonal symmetry is the two-dimensional scattering pattern from oriented samples showing six principal peaks all separated by an azimuthal angle of 60° [6].

One should consider the possibility that the instability predicted by Pereira could be an artifact of his particular implementation of SST [8]. In general, SST calculations are supplemented with various simplifying approximations [9]. For example, the implementation used by Pereira requires an assumed interfacial shape (e.g., an ellipse), rather than obtaining the detailed shape through minimization of the free energy. Nevertheless, since this particular approximation overestimates the free energy of a deformed unit cell, it should favor $\Lambda = 1$. Another approximation in his SST implementation is that the connectivity of the *A* and *B* blocks is not enforced at the interface, causing it to underestimate the stretching energy. The resulting inaccuracy should increase as the unit cell becomes less symmetrical, i.e., as Λ deviates from 1. Hence, this latter approximation could lead to an erroneous instability in the hexagonal symmetry.

Likhtman and Semenov [10] have introduced an improved version of SST that enforces the connectivity of the

blocks as well as minimizes the free energy with respect to the interfacial shape, but it is relatively complicated to apply. Less accurate but simpler to implement is an approach introduced by Olmsted and Milner [11], where the connectivity is enforced by subdividing the unit cell into infinitesimal wedges. To confirm our expectations, we implement this latter algorithm.

The Olmsted-Milner approach still requires us to specify an interfacial shape. In the interest of providing the most honest test of Ref. [1], we select the same identical interfacial shape. That is we choose an elliptical interface that deforms affinely along with the Wigner-Seitz unit cell such that they both maintain the same aspect ratio, Λ (see the diagram in Fig. 1). Wedges are then constructed emerging from the

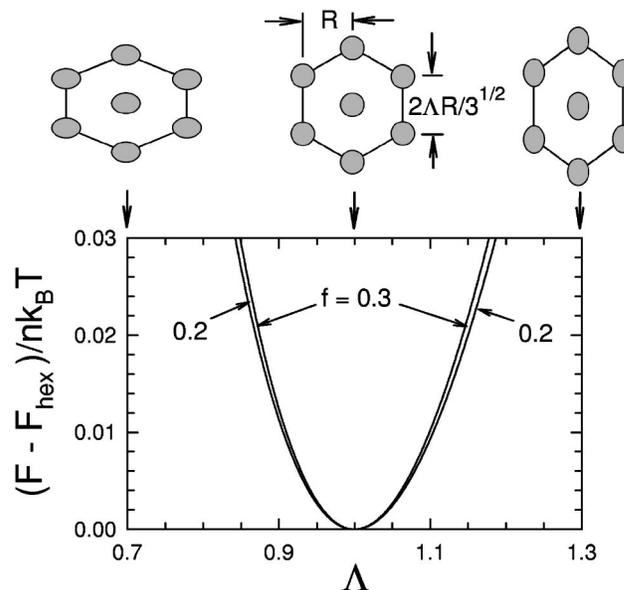


FIG. 1. Free energy F of the cylindrical phase as a function of the unit cell aspect ratio, Λ , plotted for two copolymer compositions, f , at a segregation of $\chi N = 40$. The curves are calculated using the SST of Olmsted and Milner [11], assuming that the interface deforms affinely along with the unit cell as depicted in the diagrams above. For purposes of comparison, the free energy F_{hex} of a hexagonal cylindrical phase (i.e., $\Lambda = 1$) has been subtracted from each curve.

center of the A domain with straight edges that kink only at the A - B interface, so that the fraction of the wedge in the A domain matches the A volume fraction, f , of the molecule. Note that because the unit cell and interface deform together affinely, the wedges do as well. Within the Olmsted-Milner formalism, the free energy for this geometry is given exactly by the simple expression,

$$\frac{F}{nk_B T} = (\alpha_A + \alpha_B)(1 + \Lambda^2) \left(\frac{R}{aN^{1/2}} \right)^2 + 2E(\sqrt{1 - \Lambda^{-2}}) \times \left(\frac{f\chi N}{3\sqrt{3}\pi} \right)^{1/2} \left(\frac{R}{aN^{1/2}} \right)^{-1}, \quad (1)$$

where the size of the unit cell, R , is defined in Fig. 1. The interfacial energy term, which involves a complete elliptical integral of the second kind, remains precisely the same as in Ref. [1]. However, due to our alternative treatment combined with the symmetry of the unit cell, the affine deformation of the wedges, and the fact that the field acting on the chains is parabolic, our stretching energy term takes on a much simpler form involving one coefficient for each domain [12]. The minority A domain can be treated analytically to give $\alpha_A = \pi\sqrt{3}/16$, but the coefficient for the majority B domain must be calculated numerically. For $f=0.2$ we obtain $\alpha_B = 0.31657$, whereas for $f=0.3$ we calculate $\alpha_B = 0.23577$. The resulting free energy curves minimized with respect to R are plotted in Fig. 1 as a function of deformation, Λ , for both compositions. In each case, the minimum occurs precisely at $\Lambda = 1$ corresponding to perfect hexagonal symmetry.

Ultimately, the most accurate method available for predicting the free energy of a block copolymer melt is self-consistent field theory (SCFT) [13]. This method relaxes the

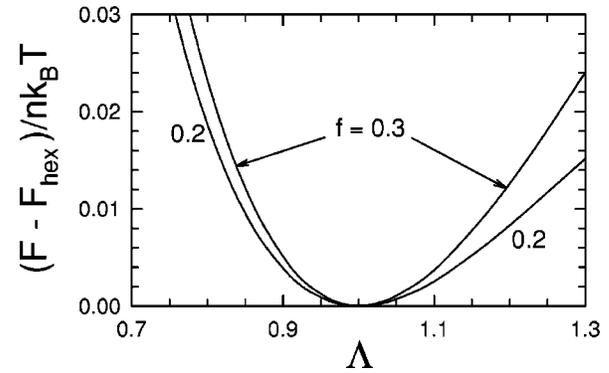


FIG. 2. An analogous plot to that of Fig. 1, but calculated using SCFT.

strong-stretching assumption in SST as well as doing away with all the supplementary approximations [9]. Figure 2 displays the equivalent free energy curves to those in Fig. 1, but this time calculated using SCFT. These numerical calculations confirm that, in each case, the minimum occurs at $\Lambda = 1 \pm 10^{-4}$, consistent with perfect hexagonal symmetry. Notice, however, that the SCFT curves in Fig. 2 are notably shallower than the ones based on the Olmsted-Milner implementation of SST. This can be attributed to the fact that the SST does not minimize the free energy with respect to interfacial shape whereas the SCFT does.

In conclusion, we used an advanced SST as well as SCFT to demonstrate that the hexagonal unit cell of the cylindrical phase is stable contrary to the predictions of Ref. [1]. Furthermore, this demonstration highlights the need for theoretical calculations to enforce the connectivity of the block copolymer chains. Naturally, it also calls into question the reliability other predictions based on the simplified SST method [8], such as the thin film results in Ref. [1].

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