PHYSICAL REVIEW E **67**, 023802 (2003)

Reply to "Comment on 'Cylindrical phase of block copolymers: Stability of circular configuration to elliptical distortions and thin film morphologies' "

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(Received 22 January 2002; revised manuscript received 3 December 2002; published 27 February 2003)

The result of Pereira [Phys. Rev. E **63**, 061809 (2001)] does not contradict previous work, but rather complements it. Both this work and previous work show there is no reason to suspect that a circular interface in a hexagonal Wigner-Seitz cell is stable to small perturbations, whether they are hexagonal or elliptical. The elliptical perturbation is on the downward energy pathway from a perfectly circular interface to a hexagonally modulated interface. Finally, my thin film conclusions are shown to be valid using an independent method.

DOI: 10.1103/PhysRevE.67.023802　　PACS number(s): 61.41.+e, 68.03.Cd, 68.60.−p

In Ref. [1], a stability analysis for the cylindrical phase of an AB diblock copolymer melt was made, using the Likhtman-Semenov (LS) method [2], in the strong segregation limit (SSL). We found that the perfectly circular interface was unstable to small elliptical perturbations. Matsen, in the preceding Comment [3], claims this result is incorrect and attempts to use two methods to back his claim. The first method is an Olmsted-Milner [5] calculation, which is not correctly implemented. (I shall detail later why the implementation is incorrect.) The second method is a self-consistent field theory (SCFT) calculation, on which I shall focus my discussion. To understand the discrepancy between Matsen's SCFT calculation and the result in Ref. [1], it is extremely important to note that Matsen's analysis and the analysis in Ref. [1] do *not* strictly address the same issue. The SSL theory used in Ref. [1] compares the free energies of only two different geometries; (i) a perfectly circular AB interface with a corresponding isotropic, hexagonal Wigner-Seitz (WS) cell and (ii) an elliptical AB interface with a corresponding anisotropic, hexagonal WS cell. The SCFT, on the other hand, has greater latitude and can sample a wider variety of possible geometries. As a result, the SCFT finds that the optimal geometry the AB interface has is of the form $r = r_0[1+\delta\cos(6\theta)]$, i.e., an interface which is predominantly circular but has a sixfold (hexagonal) perturbation. For Matsen's analysis, at $\chi N = 40$, the perturbation δ is $\approx 0.03\%$ but grows by an order of magnitude in the limit of $\chi N \rightarrow \infty$ [4]. So it is clear from Matsen's own work that the circular interface is not the optimal shape for the AB interface. The analysis in Ref. [1] is a stability analysis on the perfectly circular interface. Given that the hexagonally modulated interface already has a lower energy than a circular interface, it is not difficult to see why an elliptically perturbed interface may also have a lower energy, especially since, in a small way, it begins to resemble the hexagonal modulation. Of course I have not said anything about the stability of the elliptical geometry to, for example, the geometry obtained from the SCFT, i.e., a perturbed circle of the form $r = r_0[1+\delta\cos(6\theta)]$. It is most probably the case that this geometry has a lower free energy than the elliptical geometry. Furthermore, Matsen has implied that the analysis in Ref. [1] is incorrect because there has been no experimental observations of such distortions. There is a very simple explanation for this—the elliptical geometry is stable compared to the perfectly circular geometry but is not stable to the perturbed circular geometry, i.e., $r = r_0[1+\delta\cos(6\theta)]$.

Given the above, the rudimentary LS method [2] used in Ref. [1] underestimates the free energy because it neglects the constraint of equality of A and B ends at the AB interface. Imposing this constraint will make the minimum of the elliptical energy move closer to $\lambda = 1$ and the actual value of this minimum will increase. Note that the actual difference between the circular and elliptical free energies is only 0.3%, so that the stability issue between elliptical and circular geometries is very delicate, most probably not easily resolvable within the accuracy of most theories. In any case, this issue seems to be of academic interest because it is clear from Matsen's work that the optimal shape is the sixfold perturbed geometry. However, using the sixfold perturbed geometry with the LS method is difficult (or in fact with any other analytic method) and therefore the simpler circular geometry for the thin film analysis was used in Ref. [1].

Matsen proceeds to comment that my conclusions for thin films are unreliable. I reject this statement. To support my view, I obtained an upper bound for the elliptical distortion free energy using the Olmsted-Milner wedge approach with the straight path approximation (SPA) [5]. The SPA assumes a hexagonal outer WS cell boundary and also a hexagonal AB interface. The AB interface, however, is a factor of $f^{1/2}$ (f is the A block fraction) smaller than the WS boundary. It is important to note that this method makes a stability analysis on a symmetrical hexagonal AB interface (not a circular AB interface) and overestimates the free energy by at least 3.5% [5]. I assume an affine deformation, as in Ref. [1], where the AB interface and the WS cell boundary have the same aspect ratio. Doing this I find the free energy is given by

$$F = \frac{2F_{hex}}{3\sqrt{3}}\left[\frac{t_x^*}{t_x}\right]\left((1+\Lambda^2/3)^{1/2} + \frac{\Lambda}{\sqrt{3}}\right) + \frac{F_{hex}}{10}\left[\frac{t_x}{t_x^*}\right]^2\left(\frac{\sqrt{3}}{\Lambda^3}\right) \times\left\{\frac{2^4}{(1+3/\Lambda^2)^2}\left[\frac{\Lambda}{2\sqrt{3}} + \frac{\sqrt{3}}{2\Lambda} + \frac{1}{9\sqrt{3}}\left(\Lambda^3 - \frac{(\Lambda^2-3)^3}{8\Lambda^3}\right)\right] + \frac{\Lambda}{\sqrt{3}}\left(1+\frac{\Lambda^2}{9}\right)\right\}, \tag{1}$$

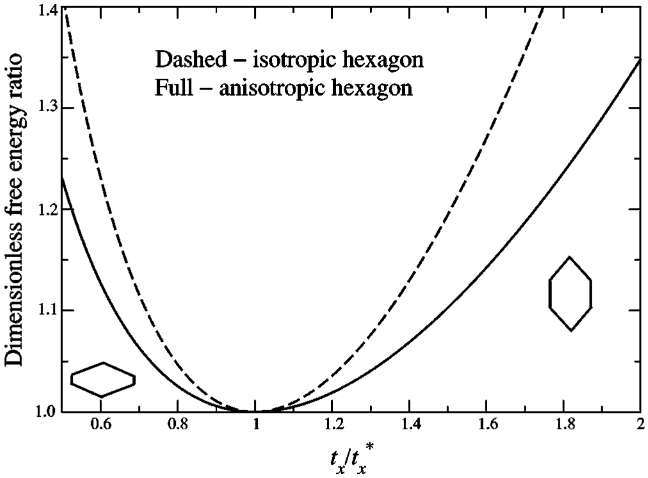

FIG. 1. Free energy of anisotropic hexagon (full curve) and isotropic hexagon (dashed curve) as a function of t_x/t_x^*, using the Olmsted-Milner wedge method, straight path approximation.

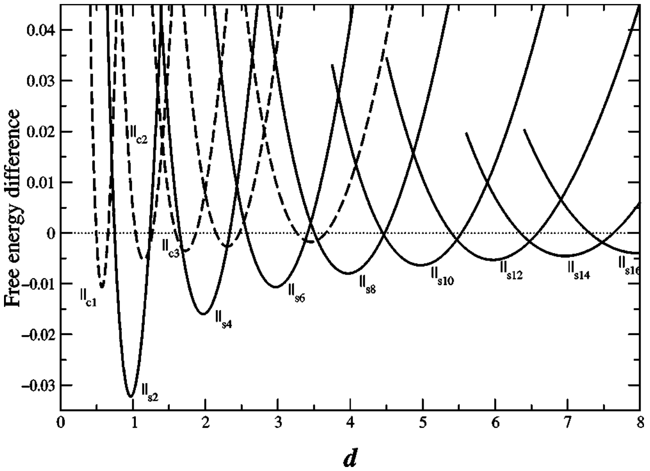

FIG. 2. Free energy difference plotted as a function of scaled film thickness $d=D/(D_{0x}/2)$ for $\Delta\gamma=(\gamma_{SB}-\gamma_{SA})/\gamma_{AB}=0.15$. Dashed curves are $\|_c$, while solid curves are for $\|_s$. The numbers correspond to number of layers. This is exactly the same calculation as Fig. 3 from Ref. [1], with the only exception being the Olmsted-Milner SPA used for the polymer energy rather than the Likthman-Semenov energy.

where $\Lambda \equiv 2\sqrt{3}t_x/t_y$, F_{hex} and $2t_x^*$ are the free energy and side length of the isotropic hexagon, respectively, and t_y is the perpendicular separation between the parallel sides of length $2t_x$. (Note, if one were using an elliptical AB interface, the eccentricity e would be related to Λ by $e^2=1-\Lambda^{-2}$ when $\Lambda>1$ and $e^2=1-\Lambda^2$ when $\Lambda<1$.) To obtain the optimal dimensions of an isotropic hexagon one writes $\Lambda=1$ and then minimizes F with respect to (t_x/t_x^*). One finds the optimal $(t_x/t_x^*)=1$. To obtain the optimal dimensions of the hexagon when the hexagon is strained $(t_x/t_x^*>1)$ or compressed $(t_x/t_x^*<1)$, we minimize F (for a particular (t_x/t_x^*)) with respect to Λ. See Fig. 1 for the results of these minimizations. From this figure it is clear that the anisotropic hexagon is preferred to isotropic hexagons when the film is strained. Hence, the main conclusion from Ref. [1] remains valid. That is, because the elliptical distortion costs, comparatively, little free energy the parallel orientation of the columns can be stabilized (relative to the perpendicular orientation) by small surface fields in favor of the minority monomer type. Figure 2 is calculated for exactly the same parameters as Fig. 3 of Ref. [1] except using the Olmsted-Milner SPA for the polymer energy rather than the LS energy. We see the parallel state is stable well beyond $d=8$, just as predicted in Ref. [1]. Note that the Olmsted-Milner SPA is an upper bound on the polymer energy and so the free energy curves have much greater curvature than the corresponding LS curves. This accounts for the small differences between the two figures. In summary, my previous predictions have been shown to be reliable, contradicting Matsen's claims.

Finally, I detail why Eq. (1) of Matsen's comment is incorrect. Matsen claims he is using the Olmsted-Milner strong-segregation theory (SST) to obtain his equation (1). In an effort to understand why he has obtained such a simple expression for the polymer stretching energy (i.e., it only has a constant and quadratic term in Λ), I have also implemented the unit cell approximation (UCA) (see Eq. (27) of Ref. [5]) and the kinked-path approximation (KPA) (see Eqs. (30)–(36) of Ref. [5]). The UCA approximation assumes a circular WS cell and also a circular AB interface. The KPA assumes an isotropic hexagonal WS cell and a circular AB interface. In both cases, extremely complicated expressions for the free energy are found (in terms of the eccentricity of the elliptic AB interface). In the KPA, one has to resort to computationally expensive numerical integration to determine the energy. Together with the SPA free energy, shown in this paper, i.e., Eq. (1), our expressions are extremely complicated functions of Λ (or eccentricity), in stark contrast to Matsen's equation (1). Matsen justifies his simple expression for the free energy with a claim that since the potential the chains experience is parabolic, the free energy must correspondingly be simple. However, one still has to integrate this potential over A and B domains which are not of the same shape. This is the source of linear and higher-order terms in Λ. Thus Matsen's equation (1) must be treated with scepticism. For an independent check, the interested reader is referred to the recent paper by Chen and Fredrickson [6], which enforces the wedge constraint for cylinders in ABC triblock copolymers. The SST calculations in this paper verify all the points made above. In particular, the elastic energy involves up to five complicated integrals as functions of the strain. Also the free energy as a function of film thickness (plotted in Figs. 7 and 8 in the paper of Chen and Fredrickson) has the same form as Figs. 2 and 3 of Ref. [1], viz., the exactly circular configuration is not the free energy minima.

Financial support from ARC QEII is acknowledged.

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