Testing strong-segregation theory against self-consistent-field theory for block copolymer melts

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We introduce a highly efficient self-consistent-field theory (SCFT) method for examining the cylindrical and spherical block copolymer morphologies using a standard unit cell approximation (UCA). The method is used to calculate the classical diblock copolymer phase boundaries deep into the strong-segregation regime, where they can be compared with recent improvements to strong-segregation theory (SST). The comparison suggests a significant discrepancy between the two theories indicating that our understanding of strongly stretched polymer brushes is still incomplete. © 2001 American Institute of Physics. [DOI: 10.1063/1.1374211]

Theories for block copolymer melts have largely developed around a single underlying model where the system is treated as incompressible, segments interact by a simple Flory–Huggins contact energy, and the entropic losses of stretching segments obey the Wiener functional. The full mean-field or rather self-consistent-field theory (SCFT) for this model was formulated by Helfand2 in 1972. Later in 1980, Leibler3 developed a simple analytical approximation for weakly segregated melts. This was followed by Semenov4 in 1985 with the development of another analytical approximation for the strong-segregation regime. Although both approximations are thought to be asymptotically exact limits of the full SCFT, this belief has only been confirmed for the Leibler calculation.5

The first attempt to establish agreement between SCFT and strong-segregation theory (SST) came several years ago when Matsen and Whitmore6 calculated the SCFT phase boundaries between the lamellar (L), cylindrical (C), and spherical (S) phases of a diblock copolymer melt into the strong-segregation regime (i.e., \(\chi N \approx 100\), where \(\chi\) is the standard Flory–Huggins parameter and \(N\) is the number of segments per copolymer). Their calculations were performed using the proper Wigner–Seitz unit cells for hexagonally packed cylinders and bcc spheres, as well as with a conventional unit cell approximation (UCA), which transforms the calculations into simpler one-dimensional problems. With the UCA, the numerical SCFT results for the L/C and C/S boundaries were accurately described by

\[
\begin{align*}
  f_{\text{L/C}} &= 0.315 + 0.84(\chi N)^{-1}, \\
  f_{\text{C/S}} &= 0.114 + 2.07(\chi N)^{-1}.
\end{align*}
\]

This raised concerns because it disagreed with the SST prediction that the diblock compositions should approach \(f_{\text{L/C}} = 0.2991\) and \(f_{\text{C/S}} = 0.1172\) as \(\chi N \to \infty\). Although the fit for \(f_{\text{C/S}}\) seemed fine, the large discrepancy for the L/C boundary suggested that a significant piece of physics had been omitted from the SST. This omission could equally affect other calculations, in particular, those for polymer brushes.8

This apparent disagreement motivated Likhtman and Semenov9 to carefully examine corrections to the SST. They concluded that the infinite-segregation prediction was correct and that the lowest-order correction should scale as \((\chi N)^{-1/3}\) rather than \((\chi N)^{-1}\) as suggested by the numerical SCFT results. When the SCFT results for \(f_{\text{L/C}}\) were plotted in terms of \((\chi N)^{-1/3}\) and compared to their more advanced SST calculation, the discrepancy was largely removed but not completely. Although the advanced SST calculation predicted values of \(f_{\text{L/C}}\) similar to those of SCFT at \(\chi N \approx 100\), there was a sizable disagreement regarding the slope of the phase boundary. Likhtman and Semenov speculated that the remaining discrepancy was due to the omission of higher-order corrections, and suggested that extending the SCFT to higher \(\chi N\) could resolve this issue.

Here we extend the previous SCFT calculations using the UCA6 by an order of magnitude in \(\chi N\) with an increased accuracy of approximately one part in a million. We accomplish this by using a basis function expansion in place of the previous real-space approach. All spatially dependent quantities, \(g(r)\), are expanded as

\[
g(r) = \sum_{i=1}^{\infty} g_i f_i(r|R),
\]

where \(r\) is the coordinate from the center of the minority domain and \(R\) is the size of their respective unit cells. For the \(L\) phase, \(R\) is half the lamellar period, and for the \(C\) and \(S\) phases, \(R\) is the radius of the unit cell. In all three cases, the first basis function is \(f_1(\rho) = 1\), while the remaining basis functions \((i > 1)\) are

\[
f_i(\rho) = \begin{cases} 
  \sqrt{2} \cos(\pi(i-1)\rho) & \text{for the } L \text{ phase,} \\
  J_0(\alpha_i\rho)/|J_0(\alpha_i)| & \text{for the } C \text{ phase,} \\
  \sqrt{3} j_0(\beta_i\rho)/|j_0(\beta_i)| & \text{for the } S \text{ phase.}
\end{cases}
\]

The coefficients, \(\alpha_i\) and \(\beta_i\), are the points, in increasing order, where the bessel function, \(J_0(x)\), and the spherical bessel function, \(j_0(x)\), have zero slope, respectively. For large \(i\), they are approximated by \(10\)
where \( m = 0, 1, \) and 2 for the \( L, C, \) and \( S \) phases, respectively. They are also eigenfunctions of the Laplacian operator, and therefore we can use the exact same formalism introduced in Ref. 11 provided we define

\[
\Gamma_{ijk} = (m+1) \int_0^1 \rho^m f_i(p) f_j(p) f_k(p) dp, \tag{8}
\]

and

\[
\lambda_i = \begin{cases} \pi^2 (i-1)^2 & \text{for the } L \text{ phase,} \\ \alpha_i^2 & \text{for the } C \text{ phase,} \\ \beta_i^2 & \text{for the } S \text{ phase.} \end{cases}
\tag{9}
\]

As always, the expansion, Eq. (3), has to be truncated to perform a calculation. We have used up to 300 basis functions, which is sufficient to assure that the numerical inaccuracy in our phase boundaries is well below \( 10^{-6} \) even at the highest segregations considered.

We have taken great care to ensure that our results are completely reliable. While our new results for the \( L/C \) boundary are in total agreement with the previous ones in Ref. 6, the results for the \( C/S \) boundary differ by up to \( 5 \times 10^{-4} \), which would be somewhat more than their estimated uncertainty although not enough to affect their conclusions. Nevertheless, this suggests the possibility of a small error in our present code. Since our present calculation employs a highly tested and utilized program, the most likely source of any error would involve the new \( \Gamma_{ijk} \) and \( \lambda_i \).

Therefore, we performed a wide range of checks to establish that these arrays were, in fact, correct. Our ultimate test involved redoing the entire SCFT calculation with the alternative expansion used in Ref. 12 for curved diblock monolayers. Although much less effective than the present approach, this independent method was able to confirm our lower segregation results (\( \chi N \approx 200 \)) up to 5 or 6 significant figures.

Our SCFT results for the \( L/C \) phase boundary are plotted in Fig. 1 with solid dots. A selection of the data points are also tabulated in Table I, along with the equilibrium domain sizes, \( R \), and free energy, \( F \), of both phases. First, we

![Fig. 1. Lamellar/cylinder phase boundary for neat diblock copolymer melts plotted against (a) \((\chi N)^{-1}\) and (b) \((\chi N)^{-1/3}\). Solid dots represent the SCFT results calculated with the UCA, and the arrows indicate the expected fit, Eq. (1), while the one in (b) is the new extrapolation based on the scaling predicted by Ref. 9.](image)

TABLE I. Classical phase boundaries with corresponding domain sizes and free energies calculated by SCFT with the UCA. \( a \) is the statistical segment length and \( n \) is the number of molecules in the melt.

<table>
<thead>
<tr>
<th>( \chi N )</th>
<th>( f_{L/C} )</th>
<th>( -\frac{R_L}{aN^2} )</th>
<th>( -\frac{R_C}{aN^2} )</th>
<th>( -\frac{F_{L/C}}{nk_BT} )</th>
<th>( f_{C/S} )</th>
<th>( -\frac{R_C}{aN^2} )</th>
<th>( -\frac{R_S}{aN^2} )</th>
<th>( -\frac{F_{C/S}}{nk_BT} )</th>
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<tr>
<td>100</td>
<td>0.323 283</td>
<td>1.1633</td>
<td>1.3141</td>
<td>7.2538</td>
<td>0.135 176</td>
<td>1.0028</td>
<td>1.0752</td>
<td>6.5547</td>
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<tr>
<td>200</td>
<td>0.319 140</td>
<td>1.3208</td>
<td>1.4832</td>
<td>9.0997</td>
<td>0.126 043</td>
<td>1.1295</td>
<td>1.1969</td>
<td>8.0683</td>
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<tr>
<td>300</td>
<td>0.317 319</td>
<td>1.4189</td>
<td>1.5889</td>
<td>10.1815</td>
<td>0.123 055</td>
<td>1.2101</td>
<td>1.2768</td>
<td>9.0639</td>
</tr>
<tr>
<td>400</td>
<td>0.316 162</td>
<td>1.4917</td>
<td>1.6675</td>
<td>11.0903</td>
<td>0.121 435</td>
<td>1.2701</td>
<td>1.3369</td>
<td>9.8295</td>
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<tr>
<td>500</td>
<td>0.315 321</td>
<td>1.5502</td>
<td>1.7307</td>
<td>11.8447</td>
<td>0.120 363</td>
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<td>600</td>
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<td>0.119 574</td>
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<tr>
<td>700</td>
<td>0.314 121</td>
<td>1.6420</td>
<td>1.8299</td>
<td>13.0730</td>
<td>0.118 957</td>
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<td>11.4839</td>
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<tr>
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<td>0.118 452</td>
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<tr>
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<td>0.117 664</td>
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<td>1.7729</td>
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<tr>
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<tr>
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<td>1.8466</td>
<td>2.0473</td>
<td>16.0023</td>
<td>0.116 583</td>
<td>1.5622</td>
<td>1.6333</td>
<td>13.8989</td>
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</table>
show the boundary as a function of \( \chi N^{-1} \) demonstrating that the earlier fit, Eq. (1), is accurate up to \( \chi N \approx 200 \) before the boundary sharply deviates away. Following the suggestion in Ref. 9, we then replot \( f_{LC} \) versus \( (\chi N)^{-1/3} \). Although the high-segregation portion of the boundary straightens out, it still retains a considerable curvature. Nevertheless, a linear extrapolation of the four points of highest segregation, the dashed line in Fig. 1(b), coincides reasonably well with the infinite-segregation prediction of \( f_{LC} = 0.2991 \). Still, the SCFT results do differ substantially from the finite-segregation correction to SST calculated by Likhtman and Semenov,9 implying that either their advanced SST has a very limited region of accuracy or that they have missed some other important effect.

The situation is much more disturbing regarding the \( C/S \) boundary shown in Fig. 2 and tabulated again in Table I. Although this time our high-segregation results are almost linear when plotted as \( f_{C/S} \) versus \( (\chi N)^{-1/3} \), our extrapolation completely misses the expected limit of \( f_{C/S} = 0.1172 \). Perhaps more troubling is the fact that the SCFT results actually overshoot the expected limit (see Table I). The \( C/S \) phase boundary would have to reverse slope in order to match the SST prediction, a suggestion that we find difficult to believe. The cylinder/gyroid boundary does reverse slope,1 but this is attributed to packing frustration,13 which is completely absent with the UCA.

In conclusion, we have developed a highly efficient SCFT numerical method for determining the classical phase boundaries of block copolymer melts using the UCA. This development was motivated by our ongoing efforts to map the extensive phase behavior of copolymer/homopolymer blends. However, it also offers the opportunity to calculate the neat diblock copolymer phase boundaries deep into the strong-segregation regime with exceptional precision, which provides a basis for testing future corrections to SST. Unfortunately, at the moment, there appears to exist a significant discrepancy between SCFT and SST. Hopefully, this will motivate a further re-examination of the SST.

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3L. Leibler, Macromolecules 13, 1602 (1980).
7These limits ignore the effect of exclusion zones, but according to Ref. 6 this is insignificant.