Accurate diblock copolymer phase boundaries at strong segregations

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We examine the lamellar/cylinder and cylinder/sphere phase boundaries for strongly segregated diblock copolymer melts using self-consistent-field theory (SCFT) and the standard Gaussian chain model. Calculations are performed with and without the conventional unit-cell approximation (UCA). We find that for strongly segregated melts, the UCA simply produces a small constant shift in each of the phase boundaries. Furthermore, the boundaries are found to be linear at strong segregations when plotted versus $(\chi N)^{-1}$, which allows for accurate extrapolations to $\chi N=\infty$. Our calculations using the UCA allow direct comparisons to strong-segregation theory (SST), which is accepted as the $\chi N=\infty$ limit of SCFT. A significant discrepancy between the SST and SCFT results indicate otherwise, suggesting that the present formulation of SST is incomplete. © *1996 American Institute of Physics.* [S0021-9606(96)50945-1]

AB diblock copolymer melts have received considerable attention because immiscibility between their *A* and *B* blocks induces self-assembly into various ordered microstructures.[1,2] The immiscibility is controlled by the product χN, where χ is the Flory–Huggins interaction parameter and N is the polymerization index of the molecule. The geometry of the microstructure is largely controlled by the volume fraction f of the *A* block. In reality, conformational asymmetry between *A* and *B* segments plays a significant role in determining the geometry.[1,3] However, as in most theoretical work, this study is limited to conformationally symmetric diblocks, where *A* and *B* segments have equal statistical lengths, a, when defined on an equal volume basis. With developments in self-consistent-field theory (SCFT),[4] mean-field phase boundaries have been accurately determined from the weak- to the strong-segregation regime.[5] At strong segregations, both experimental[6,7] and theoretical[5,8–11] evidence suggest that only the classical phases, lamellae (L), hexagonally packed cylinders (C), and body-centered-cubic arranged spheres (S), are stable. For highly asymmetric diblocks ($f\sim 0$ or 1), close-packed spheres are predicted,[5,12] but we will not be concerned with that region of the phase diagram. The aim of this study is to accurately extend the L/C and C/S phase boundaries to the $\chi N=\infty$ limit, and to quantitatively determine the effect of the conventional unit-cell approximation (UCA) discussed below. Results presented here are far more accurate than earlier ones obtained with density-functional theory.[13]

According to our present understanding,[9] strong-segregation theory (SST)[14] provides the $\chi N=\infty$ limit of SCFT. An attractive feature of this theory is that it produces analytic expressions for the quantities of interest, and provides intuitive explanations for the phase behavior. However, with this theory only the L phase can be treated exactly. To cope with the C and S phases, the unit-cell approximation (UCA) is employed, where the Wigner–Seitz cells are replaced by circular and spherical cells, respectively.[15] With that, the transitions are predicted at $f_{L/C}=0.2991$ and $f_{C/S}=0.1172$.[8,9] (For conformationally symmetric diblocks, the phase diagram is symmetric about $f=\frac{1}{2}$, and so we restrict our attention to $f<\frac{1}{2}$.) In addition to the UCA, this calculation ignores exclusion zones in the corona of the cylindrical and spherical units. As a result, an unphysical region occurs where the population of chain ends is negative.[8–10] A proper treatment prohibits this, and instead an exclusion zone occurs where the population of chain ends is identically zero.[16] This raises the free energy of the C and S phases very slightly. We find that it shifts the L/C transition by a small amount, -8.5×10^{-5}, to $f_{L/C}=0.2990$. We have not explicitly determined the effect on the C/S boundary, but it is presumably of the same magnitude.

In this Communication, SCFT phase boundaries are evaluated at strong segregations and extrapolated to the $\chi N=\infty$ limit. Calculations are performed with and without the UCA. Those with the UCA[17] are expected to extrapolate to the above SST limits, while those without it[18] provide accurate estimates of the exact mean-field boundaries. Our results produce compelling extrapolations for both phase boundaries. However, the results for the L/C boundary appear inconsistent with the SST prediction, indicating that SST is not the true $\chi N=\infty$ limit of SCFT. Although we are not presently able to explain this, we provide data that may help in future efforts to correct SST.

Our results for the L/C transitions are plotted in Fig. 1. In this case, the full SCFT calculation can be extended further than the one using the UCA. A linear fit to the points from the full SCFT for $\chi N=100$ to 180 is shown with a solid line. The line deviates from each fitted point by less than 0.0001, which is approximately the same as our numerical accuracy. The fit provides a convincing extrapolation to $f_{L/C}=0.3099$ at the $\chi N=\infty$ limit. Clearly, the extrapolation is good for $\chi N<100$. We have fit our data to other as well as

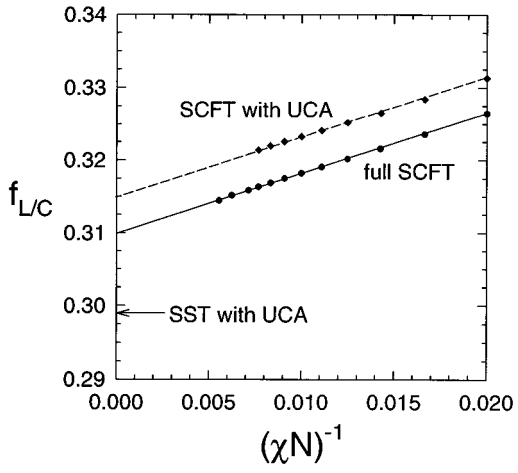

FIG. 1. Lamellar/cylinder transitions calculated by SCFT. Points on the boundary obtained with and without the UCA are denoted using diamonds and circles, respectively. The solid line represents a linear fit to the circles for $\chi N=100$ to 180. The dashed line is obtained by shifting the solid line by 0.0050. The arrow indicates the expected extrapolation of the dashed line based on SST.

more general functional forms, such as $f_{L/C}=c_0+c_1(\chi N)^{-d_1}+c_2(\chi N)^{-d_2}$, where c_0, c_1, c_2, d_1, and d_2 are fitting parameters. They produced no significant improvement in the fit and only affected the $\chi N=\infty$ extrapolation by amounts of order 0.0002. The difference between our transitions with and without the UCA is consistently 0.0050 ± 0.0001 over the range $50\leqslant\chi N\leqslant 130$. The dashed line in Fig. 1, obtained by shifting the solid line an amount 0.0050, agrees with our UCA results to within 0.0001. Based on this, we estimate that with the UCA, the L/C boundary approaches $f_{L/C}=0.3149\pm 0.0003$ as $\chi N\rightarrow\infty$. This is in sharp disagreement with the SST prediction of $f_{L/C}=0.2990$.

Following an analogous procedure for the C/S transitions, we obtain the results plotted in Fig. 2. This time, the calculation using the UCA could be extended further than the one without it. Therefore, we make a linear fit to the former

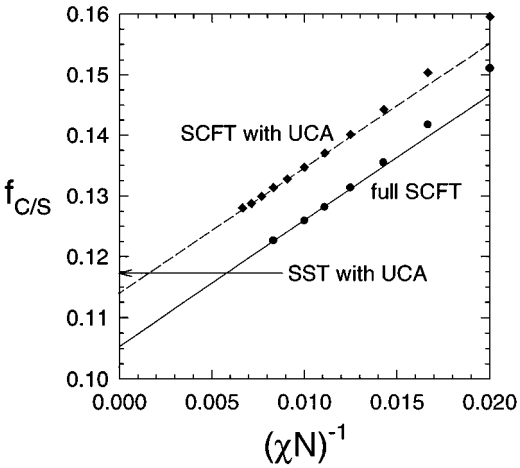

FIG. 2. Similar to Fig. 1, except that it is for the cylinder/sphere boundary. In this case, the dashed line is fit to the diamonds for $\chi N=90$ to 140, and the solid line is obtained by shifting it an amount -0.0087.

(the dashed line in Fig. 2) using the points from $\chi N=90$ to 140. Again, all the points used in the fit lie within 0.0001 of the line. Here, the extrapolation is to $f_{C/S}=0.1140$ as compared to $f_{C/S}=0.1172$ predicted by SST. Our data exhibit a significant curvature at the lower segregations. By examining fits with functional forms that allow for this, we estimate an uncertainty of 0.002 in our extrapolation. In this case, the SCFT and SST appear to be consistent. We note that the data points obtained with and without the UCA differ by 0.0087 ± 0.0001 over the range $50\leqslant\chi N\leqslant 120$. Shifting the dashed line in Fig. 2 by 0.0087 produces the solid line, which lies within 0.0001 of all the data points for $\chi N\geqslant 90$ calculated with the full SCFT. This line, which represents our best estimate of the C/S boundary at strong segregations, extrapolates to $f_{C/S}=0.1053$.

Numerical inaccuracy prevents us from determining $f_{L/C}$ and $f_{C/S}$ to an arbitrary precision. Nevertheless, we are confident of at least the four significant digits quoted in Tables I and II except for two points. With the UCA, difficulties in obtaining a convergent solution to the self-consistent-field equation restricted the $\chi N=150$ data point along the C/S boundary to three significant figures. For this reason, that point was omitted from our fit. With the full SCFT calculation, the finite number (450) of independent Fourier components used to represent spatial quantities also limited the $\chi N=120$ data point on the C/S boundary to three significant figures. In addition to the issue of numerical accuracy, there could be a concern over numerical errors. Our two programs, one that implements the UCA and the other that does not, were written and tested independently. As illustrated in Ref. 17, the program using the UCA compares accurately to the RPA[19] at weak segregations. At strong segregations, it agrees well with the Helfand-Wasserman calculation,[20] which implements a narrow-interface approximation (NIA) in addition to the UCA. Likewise, we confirmed that the program for the full SCFT calculation produced results convergent with the RPA. We note that both programs produced identical results for the lamellar microstructure. Further support for our numerics is that our estimated shift of 0.0050 in $f_{L/C}$ due to the UCA is in good agreement with the shift of 0.0058 predicted by Ref. 10. We note that an earlier and less accurate SST calculation[21] predicted a shift of twice that.

In an effort to isolate the reason for the apparent failure of the SST, we have examined the characteristic dimensions of the L, C, and S phases. Results are provided in Tables I and II. The dimensions listed include the lamellar spacing D_L, the spacing between cylinders D_C, the nearest-neighbor distance between spheres D_S, and the width of the internal interface w. We define the interface as the locus where the A-segment volume fraction, $\phi_A(\mathbf{r})$, is 0.5. The width is defined as $w=|\mathbf{n}\cdot\nabla\phi_A(\mathbf{r})|^{-1}$ evaluated at the interface, where $\mathbf{n}$ is a unit vector normal to it. The variation in w over the internal interface is negligible for each microstructure, and furthermore, the variation in w between the microstructures is small ($\pm 0.002aN^{1/2}$). For that reason, only one representative width w is provided at each transition in Tables I and II. When using the UCA, we obtain D_C and D_S from the

TABLE I. Data for the lamellar/cylinder phase boundary.[a]

	Full SCFT				SCFT with UCA			
χN	$f_{L/C}$	D_L	D_C	w	$f_{L/C}$	D_L	D_C	w
180	0.3145	2.590	2.748	0.072				
160	0.3151	2.535	2.693	0.077				
140	0.3159	2.475	2.631	0.083				
120	0.3169	2.406	2.561	0.091	0.3220	2.409	2.587	0.091
100	0.3182	2.326	2.480	0.100	0.3233	2.328	2.504	0.101
80	0.3202	2.229	2.383	0.114	0.3252	2.230	2.405	0.114
70	0.3216	2.171	2.325	0.123	0.3265	2.173	2.347	0.123
60	0.3235	2.105	2.260	0.135	0.3284	2.107	2.280	0.135
50	0.3264	2.028	2.183	0.151	0.3313	2.029	2.203	0.151

[a]The lamellar spacing D_L, cylinder spacing D_C, and interfacial width w are provided in units of $aN^{1/2}$, the RMS end-to-end length of an unperturbed chain.

radii, R_C and R_S, of the circular and spherical unit cells, respectively, by equating the cell volumes; i.e., $D_C=(4\pi^2/3)^{1/4}R_C$ and $D_S=(3\pi^2)^{1/6}R_S$. The small differences between results using the UCA and those not using it are largely attributable to the shifts in the phase boundaries. At strong segregations, our SCFT domain spacings compare well to the predictions extracted from the SST calculation in Ref. 8. Although our interfacial widths are in poor agreement with the SST prediction, $w/aN^{1/2}=2/(6\chi N)^{1/2}$,[14] they agree reasonably with an improved expression in Ref. 22. Therefore, these comparisons provide no clear indication why the SST fails to match the SCFT prediction for the L/C boundary, warranting a more in depth study.

Previous studies[22,23] have examined finite-segregation corrections to SST, and, in general, very large degrees of segregation (i.e., $\chi N\sim 10^5$) are required before these corrections become negligible.[5,23] Even with them, quantities such as the self-consistent fields, the interfacial widths, and the various segment distributions show only modest agreement with SCFT for the degrees of segregation examined here. As a result, comparisons of these quantities are unable to detect a discrepancy of the size that we are searching for. Presumably our examination of the phase boundaries is sufficiently sensitive because finite-segregation corrections largely cancel when comparing the free energies of two phases. For example, the SST phase boundaries are unaffected by inaccuracies in the interfacial tension. From our experience, we doubt that further efforts to extend SCFT results to stronger segregation will be useful in isolating the apparent discrepancy. If it exists, it will likely be identified by performing a more thorough and systematic treatment of finite-segregation corrections to the SST.

In summary, we have extrapolated the lamellar/cylinder and cylinder/sphere phase boundaries to infinite segregation using SCFT. In this limit, the transitions are predicted to occur at

$$f_{L/C}\approx 0.310+0.84(\chi N)^{-1}, \tag{1}$$

$$f_{C/S}\approx 0.105+2.07(\chi N)^{-1}. \tag{2}$$

For $\chi N\geqslant 50$, the conventional unit-cell approximation (UCA) simply shifts the L/C and C/S transitions by 0.0050 ± 0.0001 and 0.0087 ± 0.0001, respectively. With the UCA, we predict $\chi N=\infty$ limits of 0.3149 ± 0.0003 and 0.1140 ± 0.0020 for the two transitions, which can be compared to the SST predictions of 0.2990 and 0.1172, respectively. Although SCFT and SST are consistent for the C/S transition, there appears to be a sizable disagreement for the L/C boundary. Conceivably, the SCFT boundary in Fig. 1 is strongly curved beyond the degrees of segregation accessible to us. Alternatively, SST is not the true $\chi N=\infty$ limit of SCFT. This would imply that our present understanding of strongly segregated block copolymers is incomplete and that SST needs to be corrected. In either case, the discrepancy

TABLE II. Data for the cylinder/sphere phase boundary.[a]

	Full SCFT				SCFT with UCA			
χN	$f_{C/S}$	D_C	D_S	w	$f_{C/S}$	D_C	D_S	w
150					0.1280	2.046	2.009	0.087
140					0.1288	2.020	1.987	0.090
130					0.1299	1.994	1.958	0.094
120	0.1226	1.924	1.881	0.097	0.1314	1.968	1.937	0.098
100	0.1259	1.864	1.824	0.109	0.1347	1.908	1.890	0.109
80	0.1315	1.796	1.767	0.125	0.1401	1.839	1.832	0.125
70	0.1355	1.760	1.739	0.137	0.1443	1.801	1.800	0.136
60	0.1417	1.723	1.710	0.152	0.1504	1.761	1.771	0.151
50	0.1511	1.686	1.686	0.173	0.1596	1.720	1.744	0.171

[a]The cylinder spacing D_C, nearest-neighbor sphere spacing D_S, and interfacial width w are provided in units of $aN^{1/2}$, the RMS end-to-end length of an unperturbed chain.

that we report for the L/C transition is quite large, three times that produced by the unit-cell approximation and many times that resulting from the exclusion zones. Considering that the free energy differences among phases are small along the L/C transition, there is a clear possibility that incorrect conclusions may be drawn from SST calculations involving complex phase behavior.[8–10,24]

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