

## Stability of the Gyroid Phase in Diblock Copolymers at Strong Segregation

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The self-assembly behavior of linear AB diblock copolymers has been studied extensively over the past three decades, from both experimental and theoretical perspectives.<sup>1–25</sup> In the canonical theory, two independent parameters, the copolymer composition,  $f$ , and the degree of segregation,  $\chi N$ , govern the selection of the stable phase. While the three classical phases—lamellae (L), hexagonally packed cylinders (H), and body-centered spheres (Q<sup>229</sup>)—occupy the majority of the phase diagram, the double-gyroid phase (Q<sup>230</sup>), which occurs over only a narrow range of  $f$ , has occupied a disproportionate amount of researchers' attention.<sup>18–25</sup> The intriguing topology of this network structure has inspired a diverse array of potential applications ranging from high-performance separation membranes to photonic crystals.

Unfortunately, the practical applicability of Q<sup>230</sup> in the AB system appears limited due to the question of the stability of the phase in the strong-segregation regime. The majority of experimental reports of Q<sup>230</sup> involved specimens prepared in the weak-to-intermediate segregation regime ( $10 < \chi N < 40$ ).<sup>18–21</sup> In addition, many of these tended to form hexagonally perforated lamellae (HPL) for larger  $\chi N$ , although this phase was later shown to be metastable.<sup>15,16,20,26</sup> Moreover, studies that did in fact report Q<sup>230</sup> at stronger segregation were prepared by solvent-casting, which is known to encourage the formation of kinetically trapped structures.<sup>22,24,27–29</sup>

The theoretical community has also presented discouraging evidence. Olmsted and Milner<sup>30,31</sup> argued using the strong-segregation theory (SST) of Semenov<sup>7</sup> that Q<sup>230</sup> is unstable with respect to the classical phases, although this calculation imposed a wedge-shaped interfacial geometry that may be unrealistic; Likhtman and Semenov<sup>32</sup> performed an SST calculation without assuming an interfacial geometry and concluded that bicontinuous phases were stable only in the presence of added homopolymer. In 1994, Matsen and Schick presented a powerful, fully spectral implementation of Helfand's self-consistent-field theory (SCFT)<sup>1–5</sup> that first demonstrated the stability of Q<sup>230</sup> for  $\chi N \leq 20$ .<sup>15</sup> In 1996, Matsen and Bates continued the calculation to  $\chi N = 40$ , where the sharpening of the interfaces began to require a prohibitive number of basis functions and caused numerical stability issues.<sup>16</sup> On the basis of the monotonic reduction of the Q<sup>230</sup> stability region and the SST prediction, these researchers speculated that the Q<sup>230</sup> window converged to a triple point with the classical L and H phases

near  $\chi N \sim 60$ , possibly due to excessive packing frustration induced by the narrowing interfaces.<sup>33</sup> This notion was strengthened by subsequent corrections to the original SST as well as analyses of the limiting behavior of SCFT as  $\chi N \rightarrow \infty$ .<sup>13,14,17</sup>

On the other hand, a recent experimental study by Davidock et al. presented a compelling case that Q<sup>230</sup> does in fact persist well into the strong-segregation regime using a model system designed to have minimal kinetic barriers to equilibration.<sup>34</sup> Nonetheless, such evidence must be interpreted with a degree of caution since true thermodynamic equilibrium can be difficult to achieve even in intermediately segregated experimental systems.<sup>35</sup>

In the present Communication we readdress this issue using SCFT, with the dual purpose of attending to the question of the high  $\chi N$  stability of Q<sup>230</sup> as well as showcasing significant advances in addressing the numerical hurdles encountered in solving the SCFT equations. The reader is directed elsewhere for a full description of the SCFT treatment of block copolymers.<sup>1–5,15,36,37</sup> Here, we begin with the field-theoretic Hamiltonian  $H$  for an incompressible diblock copolymer melt:<sup>36</sup>

$$\frac{H[w_+, w_-]}{nk_B T} = \frac{1}{V} \int d\mathbf{r} \left[ \frac{w_-^2}{\chi N} + w_+ \right] - \ln Q[w_+, w_-] \quad (1)$$

Here  $n$  is the number of chains,  $\chi$  is the Flory segment–segment interaction parameter,  $V$  is the system volume, and  $N$  is the number of segments per copolymer;  $w_+$  and  $w_-$  may be viewed as fluctuating pressure and exchange chemical potential fields, respectively. The pressure field enforces incompressibility, while the exchange field is conjugate to the composition pattern in the melt.  $Q$  is the single-chain partition function, which is computed according to  $Q = (1/V) \int d\mathbf{r} q(\mathbf{r}, 1)$ . The forward propagator  $q(\mathbf{r}, s)$  represents the statistical weight of segments located  $sN$  units along the chain contour at point  $\mathbf{r}$ , where  $s = 0$  represents the tail of the A block and  $s = f$  is the junction between the A and B blocks. Using the flexible Gaussian-chain model,  $q$  satisfies the modified diffusion equation (MDE):

$$\begin{aligned} \frac{\partial q(\mathbf{r}, s)}{\partial s} &= R_g^2 \nabla^2 q(\mathbf{r}, s) - w_i(\mathbf{r}) q(\mathbf{r}, s) \\ i &= A; \quad 0 \leq s < f \\ i &= B; \quad f \leq s \leq 1 \\ q(\mathbf{r}, 0) &= 1 \end{aligned} \quad (2)$$

where  $w_A = (w_+ - w_-)$ ,  $w_B = (w_+ + w_-)$ , and  $R_g$  is the unperturbed radius of gyration. The normalized segment density operators (volume fractions)  $\rho_A$  and  $\rho_B$  follow from functional derivatives of  $Q$  with respect to  $w_A$  and  $w_B$  and the familiar factorization property of  $q$ .

$$\begin{aligned} \rho_A(\mathbf{r}) &= -\frac{\delta \ln Q}{\delta w_A} = \frac{1}{VQ} \int_0^f ds q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) \\ \rho_B(\mathbf{r}) &= -\frac{\delta \ln Q}{\delta w_B} = \frac{1}{VQ} \int_f^1 ds q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) \end{aligned} \quad (3)$$

The reverse propagator,  $q^\dagger(\mathbf{r}, s)$ , obeys (2) with  $q^\dagger(\mathbf{r}, 1) = 1$ .

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Within mean-field theory, the free energy  $F$  corresponds to the Hamiltonian  $H$  evaluated at an appropriate saddle-point field configuration  $[w_+^*, w_-^*]$  in which the forces vanish, i.e.

$$\frac{\delta H}{\delta w_+} = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) - 1 = 0 \quad (4)$$

$$\frac{\delta H}{\delta w_-} = \frac{2}{\chi N} w_-(\mathbf{r}) + (\rho_B(\mathbf{r}) - \rho_A(\mathbf{r})) = 0 \quad (5)$$

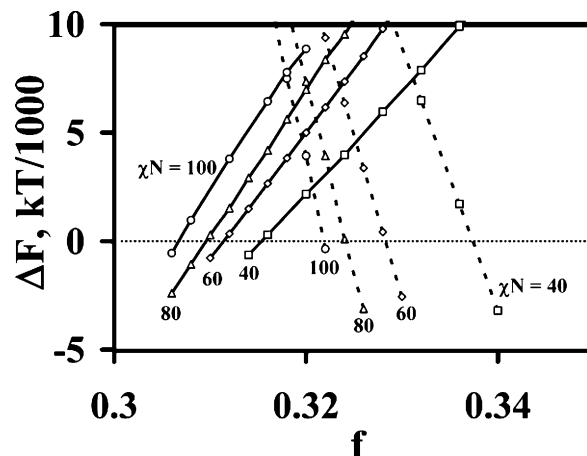
The calculation of saddle-point field configurations requires repeated evaluations of the forces, (4) and (5), which in turn through eq 3 rely on an accurate and efficient solution of the MDE (2). For strongly segregated systems, the sharpness of the A/B interface imparts a significant degree of stiffness to the SCFT equations, (4) and (5), as well as the numerical evaluation of the propagators  $q(\mathbf{r}, s)$  and  $q^i(\mathbf{r}, s)$ . We address the latter issue by discretizing in space using collocation and a plane-wave basis and solve the MDE by means of a semiimplicit method. The Laplacian operator is treated implicitly with a fourth-order backward differentiation formula (BDF4), whereas the source term is discretized explicitly using fourth-order accurate Adams–Bashford<sup>38</sup>

$$\frac{25}{12}q_{n+1} - 4q_n + 3q_{n+1} - \frac{4}{3}q_{n-2} + \frac{1}{4}q_{n-3} = \Delta s \nabla^2 q_{n+1} - \Delta s w(q_{n+1} + 4q_n - 6q_{n-1} + 4q_{n-2} - q_{n-3}) \quad (6)$$

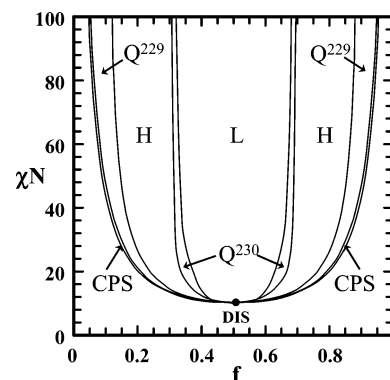
In this expression,  $q_{n+i}$  denotes  $q(\mathbf{r}, s + i\Delta s)$ , and  $\Delta s$  is the step size. The initial values required to apply this formula are obtained using backward Euler and Richardson's extrapolation. The resulting scheme is fourth-order accurate and unconditionally stable. Moreover, it produces a fast decay of high-frequency modes, which makes it an ideal candidate for stiff equations, in particular in combination with spectral collocation methods of the Fourier type.<sup>38,39</sup> Using this scheme, the average error in  $q(\mathbf{r}, 1)$  was roughly 0.001% at  $\chi N = 80$  and a step size of  $\Delta s = 0.001$ ; second-order methods, such as the operator splitting scheme of Rasmussen and Kalosakas,<sup>40</sup> required  $\Delta s < 10^{-5}$  to obtain the same level of accuracy.

We first calculated the saddle-point configuration with  $Ia\bar{3}d$  symmetry of an  $f = 0.35$  diblock at  $\chi N = 20$ , using a function proportional to the first  $Ia\bar{3}d$  harmonic (112) as the initial condition for  $w_-$ ;  $w_+$  was initially set to zero. (L and H calculations were initialized in an analogous manner.) For other coordinates in phase space the converged solution for an adjacent point served as an excellent initial condition. Saddle points were calculated using the semiimplicit Seidel relaxation method proposed by Cenicerio and Fredrickson<sup>41</sup> to update the pressure field in Fourier space while the exchange field was relaxed in real space using an explicit forward Euler scheme. The period of the unit cell was optimized concurrently with the field relaxation by minimizing the microscopic stress,<sup>42</sup> also via an explicit scheme.

Each calculation utilized a step size of  $\Delta s = 10^{-3}$  along the chain contour and a spatial resolution  $\Delta x < 0.1R_g$  (for the 3D  $Q^{230}$  simulations this amounts to  $\sim 2 \times 10^6$  plane waves). The calculation proceeded iteratively until the magnitudes of the forces, (4) and (5), were at most  $10^{-5} k_B T$  per chain. This degree of precision was reached in roughly 2500 iterations, which for a single 3D gyroid calculation required roughly 72 h of real time using 32 Intel 3.06 GHz Xeon processors in parallel. This complement of numerical approaches has proven to be an effective strategy for solving the SCF equations and remains stable even



**Figure 1.** Stability of the H and L phases with respect to  $Q^{230}$  at various degrees of segregation:  $\chi N = 40$  ( $\square$ ), 60 ( $\diamond$ ), 80 ( $\triangle$ ), and 100 ( $\circ$ ). Solid ( $\Delta F = F_H - F_{Q^{230}}$ ) and dashed ( $\Delta F = F_L - F_{Q^{230}}$ ) curves are provided to guide the eye.



**Figure 2.** Revised diblock copolymer phase diagram, adapted from ref 16, that accounts for the  $Q^{230}$  phase boundary calculations that appear in Table 1.  $Q^{229}$  and CPS refer to the spherical phases with  $Im\bar{3}m$  and close-packed (fcc or hexagonal) symmetry, respectively.

**Table 1. Phase Boundaries of  $Q^{230}$  in AB Diblocks in the Strong Segregation Regime**

$\chi N$	$f_{H/Q^{230}}$	$f_{L/Q^{230}}$	$\Delta f$
20	0.338 <sub>0</sub>	0.375 <sub>0</sub>	0.037 <sub>0</sub>
40	0.315 <sub>3</sub>	0.336 <sub>7</sub>	0.021 <sub>7</sub>
60	0.311 <sub>3</sub>	0.328 <sub>5</sub>	0.017 <sub>2</sub>
80	0.308 <sub>8</sub>	0.324 <sub>2</sub>	0.015 <sub>4</sub>
100	0.306 <sub>5</sub>	0.321 <sub>9</sub>	0.015 <sub>3</sub>

when the interfaces are both sharp and geometrically complicated as is the case in the present calculations.

In Figure 1, we plot the free energy per chain of the H and L phases with  $Q^{230}$  as the reference state. These curves show  $Q^{230}$  is stable with respect to these competing phases by no more than  $0.007 k_B T$  per chain; by comparison,  $\Delta F_{DIS-Q^{230}} \approx 14 k_B T$  at  $\chi N = 100$ , so the disordered phase is highly unstable at strong segregation. Figure 2 shows the corresponding phase boundaries, which are summarized in Table 1, on a revised diblock copolymer phase diagram. Our calculations of the composition boundaries of  $Q^{230}$  at  $\chi N = 20$  coincide precisely with those reported by Matsen and Bates<sup>16</sup> but deviate slightly at  $\chi N = 40$ , where the Matsen and Bates calculation began to encounter numerical difficulties. As  $\chi N$  is raised into the strong segregation regime, we find that the width of the stability window approaches  $\Delta f \approx 0.015$  by  $\chi N = 80$ . In Table 2, we show that this window broadens significantly with the introduction of conformational asymmetry.

The stability of complex phases such as  $Q^{230}$  in block copolymers stems, in part, from the intermediate degree of

**Table 2. Phase Boundaries of Q<sup>230</sup> in AB Diblocks with Conformational Asymmetry**

$\chi N$	$b_A/b_B^a$	$f_{H/Q^{230}}$	$f_{L/Q^{230}}$	$\Delta f$
40	0.67	0.411 <sub>2</sub>	0.438 <sub>1</sub>	0.027 <sub>0</sub>
40	1.00	0.315 <sub>3</sub>	0.336 <sub>7</sub>	0.021 <sub>7</sub>
40	1.50	0.239 <sub>4</sub>	0.265 <sub>8</sub>	0.026 <sub>4</sub>
80	0.67	0.422 <sub>1</sub>	0.442 <sub>9</sub>	0.020 <sub>8</sub>
80	1.00	0.308 <sub>8</sub>	0.324 <sub>2</sub>	0.015 <sub>4</sub>
80	1.50	0.207 <sub>9</sub>	0.234 <sub>5</sub>	0.026 <sub>6</sub>

<sup>a</sup> The ratio of the Kuhn segment length of blocks A and B, which is a measure of the conformational asymmetry.

interfacial curvature compared with neighboring L and H phases; this feature leads to an optimal degree of interfacial area and packing frustration.<sup>33</sup> This argument has been widely accepted for the presence of Q<sup>230</sup> in the diblock phase diagram for weak-to-intermediate segregation. At strong segregation, packing frustration in Q<sup>230</sup> should indeed be exacerbated by the narrowing of the interfacial thickness. This is likely the cause of the gradual contraction of the Q<sup>230</sup> region from  $\chi N = 20$  to  $\chi N = 80$ . However, our results show that near  $\chi N = 80$  this exacerbation is nearly balanced with the packing frustration of the H phase and the interfacial area of lamellae, indicating that Q<sup>230</sup> survives over a narrow range of composition deep into the strong segregation regime. Conformational asymmetry evidently broadens this range, indicating that packing frustration is alleviated more efficiently in Q<sup>230</sup> than in its competitors.

Here we caution that these results should not be construed as evidence per se that Q<sup>230</sup> is stable in the strict  $\chi N \rightarrow \infty$  limit (in the SST this limit is approached quite slowly, as  $\chi N^{-1/3}$ ),<sup>13</sup> but rather as an indication that it might be. These calculations are in accordance with recent experimental evidence<sup>34</sup> and demonstrate that the standard model for block copolymers contains the necessary physical ingredients to account for the presence of Q<sup>230</sup> at strong segregation.

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