

# Self-Assembly of Block Copolymers

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# 1 Summary

Recent advances in the application of self-consistent field theory permit the calculation of the free energy of ordered phases with any symmetry. Hence it is now possible to study within this theory the complex phases of self-assembling polymer systems starting from standard model-polymer Hamiltonians.

## 2 Introduction

Block copolymers provide simple, well-characterized, and easily controlled materials for the systematic study of self-assembly. Each molecule consists of at least two chemically joined blocks of different monomers,  $A$  and  $B$ , whose immiscibility drives the system to form structures so as to minimize contacts between the unlike monomers. This tendency to separate the monomers into relatively pure and spatially ordered regions is opposed by the loss of entropy such organization entails, just as in simpler systems. However the size of these regions is quite large due to the polymeric nature of the constituents. The size is set by a competition between the energy cost of internal interfaces separating  $A$  and  $B$  regions and the entropy cost associated with stretching polymers so as to fill space, which is required due to the near incompressibility of polymer melts. The geometry of the structure formed depends upon the relative entropy cost of stretching  $A$  and  $B$  blocks, a cost that differs due to a mismatch in their size and flexibility.

Even though this mechanism of entropy reduction is specific to polymers, the patterns of self-assembly, which the competition between enthalpy and entropy produces, are not. Indeed the structured phases observed are, for the most part, the same as those found in systems of water and lipids[1, 2] or other small amphiphilic molecules[3]. These include lamellae, cylinders packed in a hexagonal array, spheres arranged in a body-centered cubic lattice, and a bicontinuous cubic phase with

$Ia\bar{3}d$  symmetry, referred to as the gyroid. While this last structure had been seen in water/lipid systems as early as 1968[1], it was only recently observed in diblock copolymer melts[4\*, 5\*]. Another unusual structure has been reported, a perforated-lamellar phase[6, 7] in which the lamellae of minority component are pierced by a hexagonal array of holes filled with majority component. A bicontinuous, double-diamond (OBDD) phase, symmetry group  $Pn\bar{3}m$ [8], has been reported in the past but is now thought to have been a misidentified gyroid phase[9\*\*].

In addition to the experimental advantages presented by block copolymers, the theoretical program they present is relatively easy to formulate. To further simplify matters, the effect of fluctuations on polymer systems[10, 11, 12\*] is greatly reduced from that in small molecule systems. Hence mean-field, or self-consistent field, theory provides an excellent approximation in most of the parameter space. A recent advance now permits the application of this theory to an ordered phase of any space group symmetry essentially without any further approximations. This allows the detailed study of structures which had previously been extremely difficult, if not impossible, to examine, and to do so starting with standard, well-defined, microscopic models. This review focuses on the first applications of this technique to simple self-assembling systems, those of block copolymers.

### 3 Self-Consistent Field Theory

In the standard Gaussian model, a block copolymer molecule is described as a sequence of  $N$  nodes connected by springs. A fraction  $f$  of these nodes represent monomers of type  $A$ , while the remainder are of type  $B$ . Hard-core repulsive interactions between monomers are accounted for by requiring that the density of nodes be uniform; *i.e.*,  $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$ , where  $\phi_A(\mathbf{r})$  and  $\phi_B(\mathbf{r})$  are dimensionless concentrations of  $A$  and  $B$  nodes at  $\mathbf{r}$ , respectively. The remaining interactions are assumed to be local, of the form  $\chi \int \phi_A(\mathbf{r})\phi_B(\mathbf{r})d\mathbf{r}$ .

The self-consistent field theory (scft) of this system was first formulated by Edwards[13] and further developed by Helfand and coworkers[14, 15, 16]. It is derived by writing the partition function of a system of interacting polymers in terms of polymers which do not interact directly, but rather via fluctuating external fields. The representation is exact. To make the problem tractable, the fluctuating fields are approximated by static fields. The latter are chosen such that they provide the largest contribution to the partition function, which imposes self-consistent relationships between the fields and the monomer densities.

The difficulty of carrying out this program lies in obtaining solutions of the self-consistent equations which possess the complex symmetries characteristic of block copolymer microstructures. Leibler[17] recognized that near the order-disorder transition,  $A$  and  $B$  monomers would be weakly segregated and therefore  $\phi_A(\mathbf{r}) - f$  would be small and approximately proportional to a function formed from a single star of wavevectors; *i.e.* a little group of wavevectors all of the same magnitude that transform into one another under the point-group operations corresponding to the symmetry of the structure under consideration. The proportionality constant provides an order parameter with which to formulate a Landau free energy expansion and construct a phase diagram. In the opposite regime of strong segregations, Semenov[18] noted that the polymers would be strongly stretched, and therefore introduced an approximation in which polymer configurations deviating from the most probable one are ignored. Furthermore, he approximated the Wigner-Seitz unit cells of the cylindrical and spherical structures with ones of higher symmetry. This allowed him to estimate the phase boundaries between the classical lamellar, cylindrical, and spherical phases in the strong segregation limit. Recently, these calculations have been extended to the complex gyroid[19], double-diamond[19, 20\*], and perforated-lamellar[21] phases. All these structures were found to be unstable in this limit.

The problem of obtaining solutions of the self-consistent field equations for arbitrary periodic morphologies was recently solved by Matsen and Schick[22\*\*]. It was done by expanding all spatially-dependent quantities in terms of orthonormal functions with the desired symmetry. The self-consistent equations were then reexpressed in terms of the coefficients of the expansion and solved numerically without approximation other than that introduced by truncating the expansion. In contrast to the single star of wavevectors employed by Leibler[17], one can now include hundreds and perform calculations to large degrees of segregation before the effects of the truncation become significant.

## 4 *AB* Diblock Copolymers

This new procedure was initially applied to a melt of *AB* diblock copolymers[22\*\*]. It showed that, within the standard model, the gyroid phase is stable in agreement with experiment [4\*, 5\*, 7, 23, 24, 25\*\*]. On the other hand, the double-diamond and perforated-lamellar phases are not stable, although the latter is very close. The most recent calculation by Matsen and Bates[26\*\*] employs up to 450 orthogonal functions in the expansion permitting them to evaluate the phase boundaries to stronger segregations. The resulting phase diagram is reproduced in Fig. 1. There are two notable features: the gyroid phase becomes unstable for values of  $\chi N$  greater than about 60, consistent with experiment[25\*\*, 27], and for  $\chi N > 17.7$ , an additional phase of close-packed spheres is found in a narrow region along the order-disorder transition, as predicted earlier by Semenov[28]. A forthcoming publication by Matsen and Bates will explain the instability of the double-diamond and perforated-lamellar phases as well as the disappearance of the gyroid phase at strong segregations. In Fig. 1, the diblocks are assumed to be conformationally symmetric, where *A* and *B* segments have the same statistical length. This produces a diagram symmetric about  $f = 1/2$ , whereas real experimental phase diagrams are some-

what asymmetric[25\*\*]. Properly accounting for the asymmetric segment lengths shifts the phase boundaries[29, 30, 31], producing agreement between theory and experiment[32, 33].

Several scft calculations have been performed at large  $\chi N$  providing the opportunity to test the strong segregation theory (sst)[18, 34, 35\*, 36]. Comparison of domain spacings and interfacial widths[26\*\*] indicates that sst becomes valid at about  $\chi N \sim 100$ . However, a more detailed look at the amount of interpenetration of diblocks originating from adjacent interfaces of a lamellar structure[37\*] has demonstrated that the strong-stretching assumption employed in the sst requires  $\chi N$  to exceed 1000. The most recent test[38\*] has suggested that even in the infinite  $\chi N$  limit, the sst is somewhat inaccurate. The lamellar/cylinder and cylinder/sphere transitions calculated within the sst using the additional approximation of high symmetry unit cells[35\*, 36] occur at  $f_{L/C} = 0.2990$  and  $f_{C/S} = 0.1172$ , respectively. Assuming the same unit cell approximation and otherwise solving the full scft, Matsen and Whitmore[38\*] find  $f_{L/C} = 0.3149 \pm 0.0003$  and  $f_{C/S} = 0.1140 \pm 0.0020$ . While the agreement for  $f_{C/S}$  is good, the lack of agreement for  $f_{L/C}$  indicates that something has been overlooked either in the formulation or application of the sst. When the proper unit cells are used, the full scft gives  $f_{L/C} \approx 0.310 + 0.84(\chi N)^{-1}$  and  $f_{C/S} \approx 0.105 + 2.07(\chi N)^{-1}$ [38\*].

There are many extensions to the above calculations which can be contemplated, such as polydispersity[39], compressibility[40], and crystallinity[41\*, 42, 43]. One effect which promises to be interesting is molecular rigidity, an effect which can be studied within a model of wormlike chains[44\*]. Such considerations will be relevant when trying to model some of the more recent low molecular-weight block copolymers[45, 46]. Furthermore, orientational interactions are easily added to the wormlike model; those of the Maier-Saupe form bring about nematic phases[47, 48\*, 49], and lamellar phases with weak or with strong nematic ordering[48\*]. The

lamellar phases are separated by a first-order transition which ends at a critical point. They are analogous to the  $L_\alpha$  and  $L_\beta$  phases of lipid systems[50]. Unpublished experimental results of Ryan and coworkers indicate that such transitions may also be present in some block copolymers systems.

## 5 *AB* Multiblock Copolymers

The extension of scft to more elaborate architectures such as *ABA* triblocks[41\*], linear *ABAB...* multiblocks[51], combs, and starblocks[30] is straightforward provided that the molecule does not contain any closed loops. In general that is the case, but recently cyclic diblocks have been synthesized[52], which will provide a new challenge for the theory[53]. So far calculations on *AB* multiblock copolymers have not produced new features in the phase diagram. However, these calculations have not explored architectures in which either the *A* blocks or the *B* blocks are not all identical in size.

In multiblock copolymer systems, both ends of a block are constrained to an interface. The configuration of such a block must form either a bridge with its ends on distinct interfaces or a loop with both ends on the same interface. The entropy associated with this choice is small[54\*], and thus the free energy of an ordered structure is relatively unaffected by cutting such blocks in half. This is why the equilibrium behavior of multiblock copolymers is often very similar to the simple diblock. Nevertheless, the presence of bridges affects mechanical properties of the microstructure, producing rheological behavior distinct from that of diblock copolymers[55]. The first attempt to evaluate the equilibrium fraction of bridges to loops[56] applied sst and predicted the number of bridges to be small. A subsequent finite segregation calculation[57] showed that for reasonable conditions the fraction of bridges is about 40% in the lamellar morphology. The discrepancy between these predictions was resolved by Matsen[54\*] showing that the original calculation did

not properly treat the entropy associated with bridging and looping. Subsequently, experiments have confirmed the predicted bridging fraction of 40%[58]. These calculations have yet to be extended to other morphologies, nor has the effect of added homopolymer or solvent been addressed.

## 6 *ABC* Triblock Copolymers

The complexity increases substantially with the addition of a third chemically distinct block. Even the simplest architecture of this type, the *ABC* triblock, is unwieldy. Instead of one incompatibility parameter,  $\chi_{AB}$ , there are now three,  $\chi_{AB}$ ,  $\chi_{BC}$ , and  $\chi_{AC}$ , and instead of one fraction,  $f$ , describing the composition, there are two. This complexity is reflected in the phase diagram. In addition to ordered spherical, cylindrical, lamellar, and tricontinuous double-diamond structures analogous to those in the diblock system[59, 60, 61, 62], four phases of different morphologies were recently identified[63, 64\*, 65]. In *ABC* triblocks, the first of these exhibited cylinders of *B* at the interfaces of *AC* lamellae, the second was characterized by spheres of *B* at the same interfaces, the third consisted of *A* cylinders surrounded by rings of *B* dispersed in a matrix of *C*, and in the fourth helices of *B* were wrapped around *A* cylinders in the *C* matrix. The possibility of phases consisting of combinations of cylinders, spheres, and lamellae had previously been predicted[66]. Phase diagrams in the strong segregation limit have been calculated[64\*, 67\*], and the general dependence on the parameters is understood. There are as yet no phase diagrams showing the behavior in weak, intermediate, and strong segregation regimes, comparable to that of Fig. 1 for diblocks.



## 7 Blends of Diblock and Homopolymer

The addition of  $A$  homopolymer of polymerization index  $\alpha N$  to a system of  $AB$  diblock of index  $N$  has several dramatic effects on the stability of phases[68\*\*, 69]. A few general statements can be made. Entropy favors the mixing of the  $A$  homopolymer with the  $A$  domain of a diblock microstructure. However, providing the necessary space within the domain requires the  $A$  blocks to stretch, and this is unfavorable. When  $\alpha > 1$ , the penalty of stretching the  $A$  blocks tends to discourage mixing of homopolymer and diblock, producing phase separation. However, if  $\alpha < 1$ , entropy dominates and the two components mix readily, swelling the microstructure. This is particularly true if  $A$  forms the majority domain (*i.e.*,  $f > 1/2$ )[70, 71]. Under some conditions, this swelling can continue as long as homopolymer is added, increasing the characteristic scale of the phase without limit. This divergence in spacing is denoted complete unbinding. On increasing  $\chi N$ , the behavior of the ordered phase changes quite abruptly, with the unbinding replaced by a region of two-phase coexistence between a disordered phase and a lamellar one of finite wavelength. The transition from one behavior to another is denoted an unbinding transition, and can be either continuous or first-order[72]. For the system characterized by  $f = 1/2$  and  $\alpha = 1$ , it was found[73\*] that the unbinding transition is first-order. The consequence of the first-order nature is that for a range of  $\chi N$  somewhat less than the value at the transition, there exist two lamellar phases of different period which can coexist with one another. The coexistence line ends in a critical point. The phase diagram is shown in Fig. 2.

Another notable effect of adding homopolymer to a system of diblocks is to stabilize phases which were unstable in the pure diblock system, such as the double-diamond and perforated-lamellar structures[69]. This occurs because the homopolymer can relieve strain in the  $A$  blocks of the copolymer by occupying regions in the

microstructure which would otherwise be filled by highly stretched copolymers. Precisely because of this relief of strain, one observes a phase transition from a lamellar phase to a perforated-lamellar phase as this system is subjected to strain. This appearance of holes in the membrane with the imposition of stress has been used to model electroporation, the creation of pores in a bilayer membrane by application of an electric field[74\*]. A transition from a lamellar to a perforated-lamellar phase has been observed in blends of homopolymer and copolymer[6], and the results of the scft calculation[68\*\*, 69] are in good agreement with experiment.

The effects of adding homopolymer to a diblock system has also been examined in the strong segregation limit[75]. Again one finds two-phase separation when the  $A$  homopolymers are longer than the diblock. When the homopolymers are shorter and mix with the diblocks, their effect is to shift the boundaries between different phases significantly. Given that homopolymer increases stability by relieving strain, it is natural to consider whether complex phases could be stabilized by homopolymer in the strong segregation limit. This question has been examined by Xi and Milner[76] who conclude that the gyroid phase is stable for  $0.56 < f < 0.68$  provided that the concentration of homopolymer is optimal, ranging from 0.18 to 1.00 for the above range of  $f$ .

## 8 Ternary Mixtures of Diblock and Homopolymers

Ternary mixtures of  $AB$  diblock with  $A$  and  $B$  homopolymers is the next system in the sequence of increasing complexity. The additional  $B$  homopolymer species requires another polymerization index and molecular volume fraction to be specified. This makes for a rich phase diagram indeed. Until this year, there was relatively little theoretical work on the ordered phases of such ternary blends. One of the first such studies by Banaszak and Whitmore[77] implemented the weak segrega-

tion approximations of Leibler[17] and limited their consideration to the lamellar microstructure only. Naturally this severely restricts the parameter space in which their results are reliable. Nevertheless they could examine many interesting issues, such as how diblock bilayers characteristic of the binary system transform into monolayers as a second homopolymer species is added. Other calculations have examined the elastic properties of this monolayer for both weak[78] and strong[79] segregations.

In a forthcoming publication, Janert and Schick apply the full scft to the ternary system. Again, a few general observations can be made. From the results of the binary system, one knows that a long homopolymer added to a diblock causes a two-phase region. In the ternary system, this coexistence region can be quite extensive even if the other homopolymer is rather short. If the homopolymers are of the same index, then the region of phase separation is generally smaller when the homopolymers are short than when comparable or larger than the diblock[71]. For the shorter homopolymers, the various ordered phases, such as lamellar, cylindrical, and spherical, extend from the binary limits inward toward the axis of equal homopolymer volume fractions. These phases end at coexistence regions when the volume fraction of diblock becomes too small to compatibilize the homopolymers. The lamellar phase undergoes a complete unbinding[80]. In contrast, when all components have equal polymerization indices and the diblock is symmetric, the only ordered phases are lamellar. Furthermore, Janert and Schick have shown that this lamellar phase does not undergo a complete unbinding along the isopleth. Instead, when the diblock concentration becomes sufficiently low, it phase separates into two coexisting lamellar phases, one  $A$ -rich and the other  $B$ -rich. As the copolymer content of the system is reduced, these phases undergo complete unbinding just as they do in the two-component limit.

## 9 Binary Diblock Blends

Recent studies on mixtures of  $AB$  diblocks have showed interesting and useful behavior. Experiments involving short and long lamellar-forming diblocks revealed that phase separation occurs when the molecular weight ratio exceeds about 1:10[81, 82]. Although strong segregation theory[83\*, 84, 85] does not predict this behavior, the full scft[83\*] does. Furthermore, the full scft predicts critical molecular weight ratios, and compositions of the phase-separated lamellar structures, which are in agreement with experiment. More recent experiments illustrate this same behavior in blends of sphere-forming diblocks[86].

Further studies using sst have examined how the addition of small amounts of a low molecular weight diblock alters the phase boundaries between morphologies[87]. Another study using scft examines the phase behavior of diblocks of equal size but different composition[88]. Both these studies omitted the possibility of macrophase separation, which in the latter case is unjustified[89\*]. A more recent calculation[89\*] evaluates the two-phase region and in addition theoretically justifies a previous experimental procedure[90] based on the one-component approximation. The experimental procedure assumes that a blend of two diblocks with compositions  $f_1$  and  $f_2$  mimics a pure diblock melt of composition  $f = (1 - \phi)f_1 + \phi f_2$ , where  $\phi$  is the volume fraction of the second diblock. Not only does this greatly reduce the effort required to map out a diblock phase diagram, it provides an accurate way of achieving a desired composition  $f$ .

## 10 Externally Applied Fields

As our knowledge regarding block copolymers increases, we are able to address new issues such as how external fields affect their behavior. The most commonly studied is the application of stress[91, 92, 93], and in particular shear stresses have attracted

significant attention[94, 95, 96, 97, 98\*, 99]. When applied to the lamellar structure, domains orient in one of two directions depending on the frequency. Recently, similar behavior has been reported for the cylinder morphology[100]. Other possibilities include electric fields[48\*, 74\*, 101, 102, 103] and pressure[104, 105, 106, 107\*]. Such studies are certain to enhance our understanding of block copolymers.

## **11 Conclusions**

Complex phases of block copolymer systems can now be studied within the context of self-consistent field theory without further approximation. This is an important advance because these systems are a paradigm of self-assembly. Understanding the factors which lead to one structure rather than another will undoubtedly be relevant to other self-assembling systems as well. Applications of the technique have just begun on the simplest model systems, and will surely be generalized to explore the effects on ordered phases due to changes in architecture, sequence distribution, number of components, differences in flexibilities, and the addition of specific impurities, such as molecules of specialized function. Such studies should be particularly rewarding.

## **12 Acknowledgements**

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In this experiment, an oriented bicontinuous structure is epitaxially grown from a shear-oriented cylinder phase. By indexing small-angle neutron scattering reflections, the space group is identified as  $Ia\bar{3}d$  demonstrating the existence of the gyroid phase in block copolymer melts.

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- The authors of this work reexamine a large number of previously identified double-diamond samples. Their more careful analysis shows these samples to be inconsistent with the  $Pn\bar{3}m$  space group symmetry and instead consistent with the  $Ia\bar{3}d$  symmetry of the gyroid phase. This note presents a representative selection of their findings.
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A simple formulation of the strong segregation theory is derived which can be applied to complex structures. The simplification is achieved by relaxing the constraint that the concentration of ends from *A* and *B* blocks be equal along the internal interface.

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This letter presents the procedure for calculating the free energy of an arbitrary periodic block copolymer structure within the self-consistent field theory. The method is illustrated for diblock copolymers.

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These authors provide a succinct formulation of the strong segregation theory that can be applied to complex morphologies. We alert the reader to the fact that their expression for the interfacial area (eq. 4) is wrong and that their results have been corrected in ref.[19].

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Phase boundaries between the lamellar, cylindrical, and spherical structures are calculated using strong segregation theory (sst) and self-consistent field theory (scft). Unexpectedly, the two theories seem to disagree, suggesting there is an effect that still needs to be accounted for in the sst.

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## Figure Captions

**Fig. 1** Phase diagram of diblock copolymers calculated from self-consistent field theory. Phases are labeled L (lamellar),  $Q_{Ia\bar{3}d}$  (gyroid), H (cylindrical),  $Q_{Im\bar{3}m}$  (bcc spherical), CPS (close-packed spherical), and DIS (disordered). Dashed lines denote extrapolated phase boundaries, and the dot denotes a critical point. After ref.[26\*\*].

**Fig. 2** Phase diagram of symmetric  $AB$  diblock and  $A$  homopolymer of the same polymerization index as a function of incompatibility  $\chi N$  and copolymer volume fraction  $\phi$ . Dotted line is the locus of complete unbinding transitions; upper dot denotes an ordinary critical point, lower dot a Lifshitz critical point. After ref.[73\*].