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Ordering of Diblock Copolymer Materials on Patterned Substrates: a Single Chain in Mean Field Simulation Study

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Summary: The directed assembly of diblock copolymers on patterned substrates is a way to create nanoscopically structured materials. We study the structure and kinetics of diblock copolymers on patterned substrates by simulating a large ensemble of independent chains in an external field. This external field depends on the density created by the ensemble of molecules and it is frequently updated as to mimic the instantaneous interactions of a molecule with its neighbors. This approximate, particle-based field theoretical method allows (i) to incorporate arbitrary chain architecture (ii) to include fluctuations and (iii) the explicit propagation of the chain conformations in time permits us to study the kinetics of structure formation. The factors that control the accuracy of the method are quantitatively discussed and the reconstruction of the soft morphology at substrate patterns that deviate from the periodic morphology of the diblock in the bulk are illustrated.

Keywords: block copolymers; computer simulation; order-disorder transition; self-assembly; self-consistent field theory

Introduction

Polymeric materials comprising different components find widespread use in technical applications ranging from packaging materials (e.g., rubber-toughened polystyrene) and coatings to pattern replication on the nanoscale. Due to the low entropy of mixing multi-component materials often do not mix at the atomistic scale but form domains in which one of the components is enriched. The domain size and their spatial arrangement can be controlled by using block copolymers in which two or more incompatible components are covalently connected into a single molecule. The connectivity of the components along the backbone of the molecules prevents macroscopic phase separation, and the morphology of the domain structure is determined by the interplay between the free energy of the domain interfaces, which favors large domain sizes, and the entropy loss due to the stretching of the molecules as they fill the volume with constant density (incompressibility). Depending on the volume fraction of the two components of a diblock copolymer, one finds lamellar structures, cylindrical rods that arrange on a hexagonal lattice, spherical domains or more complex morphologies. The domain size in the bulk can be tuned by adding the corresponding homopolymers which segregate to the middle of the domains, thereby relieving some of the stretching penalty allowing for domain swelling.

Recently, diblock copolymer materials have attracted much interest because they offer the opportunity to create and/or replicate patterns on the scale of a few tens of nanometers.[1] One exposes a thin diblock copolymer film to a chemically patterned substrate that directs the assembly

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of the diblock copolymer material. If the two-dimensional substrate pattern has a "similar" length scale and symmetry as the diblock copolymer morphology in the bulk this directed assembly in thin films is able to replicate the pattern over larger areas without defects and in perfect registration.[2] Otherwise, the reconstruction of the diblock copolymer morphology at the patterned surface can create new morphologies that have no analogies in the bulk[3–5]

On these small length scales the mechanical properties of the structures, their line edge roughness, and their tolerance to minor imperfections of the pattern to be replicated become increasingly important. Diblock copolymers offer advantages because their assembly is thermodynamically driven: The interfaces between domains are rather smooth and fluctuations are controlled by the tension and rigidity of the interfaces. Moreover small defects of the underlying pattern can be compensated by the forces that drive the assembly of the diblock copolymers (in the bulk). The very same beneficial thermodynamic driving forces, however, limit the patterns that can be replicated to those that resemble bulk morphologies. This limitation can be mitigated by blending copolymers with their respective homopolymers or utilizing a mixture of copolymers with different architectures (e.g., diblock copolymers and triblock copolymers). How closely the bulk morphology and the substrate pattern have to match or how to tune the properties of the diblock copolymer material in order to achieve defect-free replication is an open question. Which new morphologies can be fabricated by reconstruction of the soft morphology at patterned surfaces also is largely unexplored.

In this manuscript we present an approximate numerical method – "Single Chain in Mean Field (SCMF)" simulations[5–7] – that enables us to study the directed assembly of diblock copolymer films on patterned substrates on large length and time scales.[8] In the next section we will briefly describe the salient characteristics of the method and illustrate its ability to describe correlations. Then, we will discuss the ordering of diblock copolymer materials on patterned substrates resembling the bulk morphology as well as the reconstruction of the morphology on surface patterns that strongly differ both in symmetry and length scale from the bulk morphology.

Single-Chain-in-Mean-Field (SCMF) Simulations

We study the directed assembly of diblock copolymer thin films on patterned substrates within the framework of a coarse-grained polymer model. This minimal model is characterized by a small number of coarse-grained parameters[9] – the end-to-end distance of the diblock chains in the molten state, R_e, and the incompatibility between the A- and B-blocks, χN. The chain conformations are described by a discretized Edwards-Hamiltonian[10]

$$\frac{H_b[r(s)]}{k_B T} = \sum_{s=1}^{N-1} \frac{3(N-1)}{2R_e^2}[r_i(s) - r_i(s+1)]^2 \quad (1)$$

where R_e^2 denotes the mean squared end-to-end distance of the polymers in a dense melt. This is the only characteristics of a Gaussian chain and R_e sets the unit length scale. The chain contour of the diblock copolymers is discretized into $N = 32$ effective segments. Each molecule is comprised of fN A-segments and (1-f)N B-segments. The space is discretized into cells with size, $\Delta L = R_e/6$. The relevant non-bonded interactions consist of the excluded volume of the effective segments and the repulsion between unlike segment species that gives rise to microphase separation:

$$\frac{H_{nb}[\phi_A, \phi_B]}{k_B T} = \frac{\rho}{N}\int_V d^3r \left(\frac{\kappa N}{2}[\phi_A + \phi_B - 1]^2 - \frac{\chi N}{4}[\phi_A - \phi_B]^2 + \Lambda N f(r)[\phi_A - \phi_B] \right) \quad (2)$$

where $\rho \equiv nN/DL_xL_y$ denotes the segment number density, D is the film thickness while L_x and L_y denote the lateral dimensions of the film.

$$\phi_A(r) = \frac{1}{\rho}\sum_{i=1}^{n_A}\sum_{s=1}^{fN}\delta(r - r_i(s)) \tag{3}$$

is the microscopic local density of A-segments. A similar expression holds for ϕ_B. The excluded volume interactions of the effective segments are modelled via a Helfand compressibility term[11] which penalizes fluctuations of the local density from its average. κ describes the inverse thermal compressibility of the segment fluid. The repulsion between unlike segments is parameterized by a Flory-Huggins parameter, χ. In our numerical calculations we utilize the values $\chi N = 37$ and $\kappa N = 50$. These values give rise to well segregated domains and strongly restrict density fluctuations. As it is common practice in self-consistent field theory the strong and harsh repulsion between the segments (hard core interactions) are replaced by weaker ones that ensure effective incompressibility not on the length scale of segments but on the scale of (a small fraction of) R_e.

The film surfaces (substrate and top surface to air/vacuum) are modelled as hard and impenetrable so that the last term in Equation (2) describes the polymer interaction with the surface pattern which is encoded via the function f(r). The integral over space in Equation (2) is discretized on a simple cubic grid. The grid spacing plays the role of the length scale of inter-segment interactions. The interactions have a cubic anisotropy and are not translationally invariant, but the segment coordinates are continuous. In the present study we assign a particle to the density of the nearest grid point but more sophisticated assignment functions can be envisioned. For typical simulation parameters a grid cell contains on the order of ten segments and calculating the interactions via the grid is about two orders of magnitude faster than employing pair-wise interactions with a similar range.[7]

Equations (1)–(3) define a particle-based model that can be studied by Monte Carlo simulations[12] This method yields the exact statistical mechanics but it is computationally expensive. Often, the particle-based model serves as a starting point for a mean field approximation. In the mean field approximation the average segment interactions are replaced by external fields that are self-consistently determined from the average density distribution generated by the molecules exposed to the external fields. This self-consistent field theory is computationally much less demanding than simulations but it neglects fluctuations.[13] The validity of the mean field approximation (or the strength of long-ranged fluctuations) is controlled by the Ginzburg number $\mathrm{Gi} \sim 1/\overline{N} = (N/\rho R_e^3)^2$. Gi is a property of the system dictated by the density and molecular weight. In scope of exploring the kinetics of microphase separation dynamic SCF (DSCF) methods have been developed. However DSCF assumes that the chain conformations are in equilibrium with the local density distribution. One also requires an Onsager coefficient that establishes the relation between the kinetics of the collective variable (i.e., density fields) and the dynamics of the underlying molecules.

In SCMF simulations one considers a large ensemble of independent molecules subjected to fluctuating, real external fields. The molecules' conformations are updated through a short Monte Carlo simulation. Subsequently, the external fields are frequently updated utilizing the instantaneous density distribution of the ensemble. The external fields represent the interactions of a molecule with its surrounding that fluctuates in space and time. If the fields followed the density instantaneously, they would faithfully describe the intermolecular interactions and the method would be exact. The failure of the external fields to mimic the instantaneous interactions constitutes the ‘‘quasi-instantaneous field approximation’’. In the simple case that the fields are frequently updated and the spatial discretization (i.e., grid spacing) is set by the statistical segment length $b = R_e/N^{1/2}$ the approximation is controlled by the parameter $1/\sqrt{N\bar{N}} = \sqrt{\mathrm{Gi}/N}$. This control parameter does not only depend on the Ginzburg number (a physical property) but also on the chain contour discretization used in the calculations (an attribute of the numerical scheme). Thus, by a suitable choice of discretization, SCMF simulations can provide accurate results (e.g., describe fluctuations) in cases where SCMF theory fails (e.g., polymeric micro-emulsions).

Utilizing local Monte Carlo moves[6] or Brownian dynamics[14,15] we describe the Rouse dynamics of polymers in a spatially inhomogeneous environment for which no analytical form of the Onsager coefficient is known. Generalizations to the dynamics of entangled chains (i.e., reptation-like motion) can be envisioned.[7] Of course, in a single chain theory the entanglement length has to be introduced "by hand" and cannot be the outcome of the simulation.

Applications

1. The correlation hole of the intermolecular pair correlation function and long-ranged bond-bond correlations

The most basic intermolecular correlations in a dense one-component polymer system stem from the fact that the dense polymeric fluid is almost incompressible.[16] On the length scales larger than the screening length ξ fluctuations of the total density are strongly suppressed. On distances $\xi < r < R_e$, the normalized probability to find any segment at a distance r from a reference segment is unity. The intermolecular pair correlation function $g_{\mathrm{inter}}(r)$, which measures the probability to find a segment of another molecule at distance r, however, is reduced. In Figure 1 a) we present the total and intermolecular pair correlation function for a dense melt of long chains. At small length scales, $r < \xi$, the total correlation function is enhanced indicating density fluctuations inside the "excluded volume blob". The SCMF simulation results are compared to the results of Monte Carlo simulations of exactly the same model and the prediction of the Random Phase Approximation[16] for Gaussian chains. All three methods quantitatively agree and describe the vanishing of the density fluctuations for $r > \xi$. The Random Phase Approximation is not able

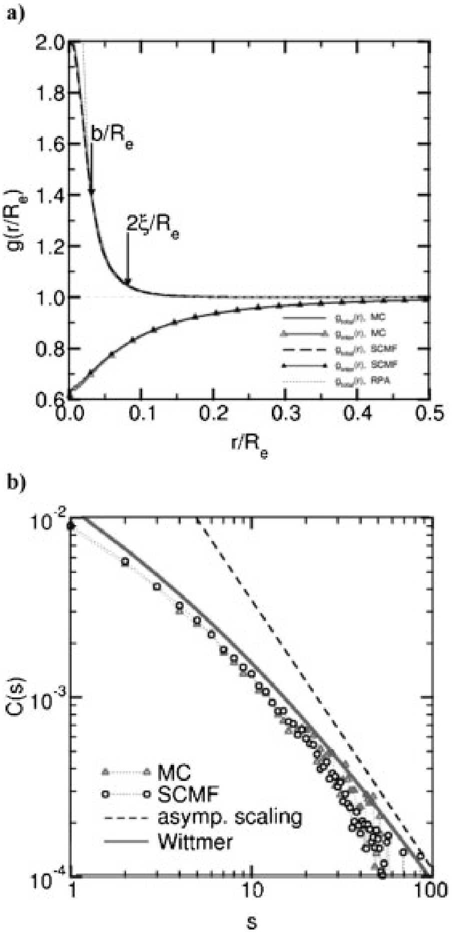

Figure 1.

a) Intra- and intermolecular pair correlation functions of a dense melt. Results from exact MC simulations, approximate SCMF simulations and Random Phase Approximation for Gaussian chains are presented. The simulations utilize chains comprised of $N = 1024$ segments. b) Decay of the correlation *C*(*s*) between bond vectors with distance s along the polymer chain contour. Both, results of MC simulations and SCMF simulations are shown and the data are compared to the prediction of the asymptotic behavior and an expression that take finite chain length effects into account (J.P. Wittmer, private communication, 2006). From Ref.7.

to describe non-trivial intermolecular correlations; both the Monte Carlo simulations as well as the approximate SCMF simulations predict a correlation hole and quantitatively agree. This correlation hole is an important property: If one intends to utilize the results of SCMF simulations to generate starting configurations for conventional Monte Carlo or molecular dynamics simulations these long-ranged intermolecular correlations will have to be duly taking into account. Moreover, the intermolecular correlations also impact the intramolecular structure giving rise to bond-bond correlations that do not decay exponentially but like a power law.[17] These long-ranged intramolecular correlations are presented in panel b) of Figure 1 where we compare the results of Monte Carlo and SCMF simulations with the asymptotic prediction and an expression that takes account of finite chain length effects.[7]

2. Ordering of a lamella-forming ternary copolymer-homopolymer blend on a nested bend pattern

Due to the independence of the molecules during the Monte Carlo simulations in the external fields, SCMF simulations are ideally suited for parallel computers. This allows us to study large systems and follow their time evolution over many Rouse times.[8] Thus, this method is suitable for exploring which substrate patterns can be reproduced by the directed assembly of diblock copolymer thin films on patterned substrates. In the following we illustrate the potential of SCMF simulations investigating the directed assembly of a symmetric AB diblock copolymer blended with the corresponding A and B homopolymers.[2] The ternary blend forms a lamellar structure in the bulk. In a thin film the morphology is dictated by a subtle interplay between the bulk thermodynamics and the substrate interactions. If the substrate pattern consists of lines whose spacing matches the bulk lamellar spacing the diblock copolymer material will perfectly replicate the substrate pattern because the properties of bulk morphology and of surface pattern are synergistic reinforcing the ordering. Substrate pattern that consists of an array of nested bends constitutes a first step towards device-oriented patterns.[2] This pattern is characterized by two length scales – the distance between the interfaces in the parallel portions of the nested bends and the larger distance of the interfaces between subsequent corners of the nested bends. The sharper the bend the larger the difference between the two length scales. In Figure 2 a) we present the morphology of the diblock copolymer material on the nested bend pattern. In agreement with experiments, the substrate pattern is replicated by the diblock copolymer material without defects. At the corners, however, the morphology at the free top film surface is slightly distorted and exhibits a structure that resembles structures observed at grain boundaries between two lamellar domains of different orientation. In the former case, however, these structures correspond to thermodynamic equilibrium and at the patterned substrates the morphology follows the pattern in every detail, i.e., the AB interface is pinned at the substrate pattern and no distortion at the corners is detectable. It is interesting to note that ternary blend is able to replicate the pattern even if the difference in the two characteristic length scales is larger than the mismatch between the period of the substrate pattern and the lamellar bulk morphology in case of a parallel line pattern. This is made possible by the redistribution of the homopolymers – they are enriched at the corners in order to selectively swell the morphology and cater for the larger distance between the interfaces. This is clearly observable in Figure 2 b) where the relative concentration of homopolymers is shown. Homopolymers are strongly enriched at the corners and the effect increases as the bends become sharper. The shorter homopolymers are also enriched at the impenetrable substrate and surface, and in the middle of the lamellae. This example demonstrates the possibility to replicate patterns that differ from the bulk morphol-

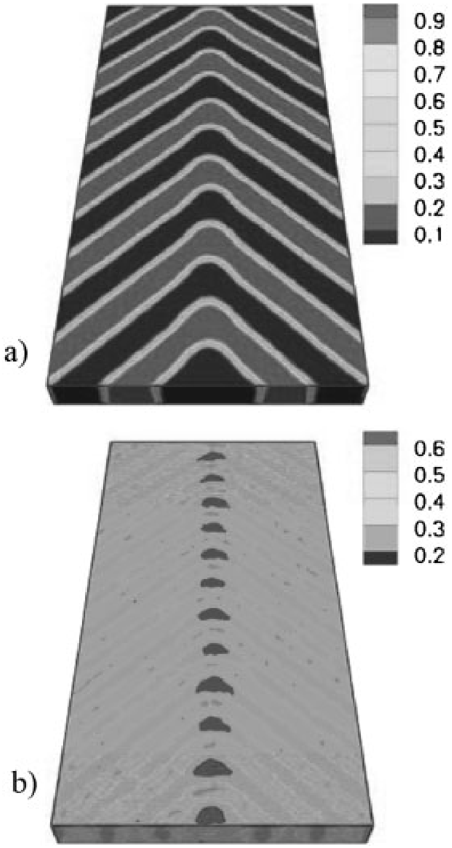

Figure 2.
Morphology of a thin diblock copolymer material on a patterned substrate that consists of an array of nested bends. The ternary mixture of a symmetric AB diblock copolymer and the corresponding homopolymers forms a lamellar structure in the bulk. Panel (a) presents the three dimensional contour plot of the composition, panel (b) shows the relative concentration of homopolymers (irrespectively of their type A or B). From Ref. 2.

ogy and comprise more than one characteristic length scale. It also illustrates that by tuning the properties of the diblock copolymer materials (e.g., the composition) it is possible to extend the range of patterns that can be replicated.

3. Directed assembly of a lamella-forming copolymer-homopolymer blend on a quadratic spot pattern

If bulk morphology and substrate pattern differ too strongly in symmetry or length scale the substrate pattern cannot be replicated by the diblock copolymer material and the morphology in a thin film is dictated by a subtle interplay between the bulk thermodynamics and the influence of the substrate pattern.[3,4] Since in these soft materials different morphologies are distinguished only by small differences of the free energy (on the order of tens of k_BT per molecule) the interaction with the substrate has a pronounced influence and the reconstruction of the morphology at the substrate can propagate rather far away from the substrate in a semi-infinite system. For the film thicknesses considered here, which are of technological relevance for pattern replication in semi-conductor industry or for filtration membranes, the reconstruction dictates the morphology throughout the entire film thickness.

In Figure 3 we present the morphology of a lamellar forming ternary blend on a substrate pattern that consists of a square array of spots attracting one component B of the diblock copolymer. For clarity only A-domains (i.e., the ones that are not preferred by the spots on the substrate) are shown light grey (yellow) and the interface between A- and B-domains is colored dark (blue). One can see that the substrate interactions are strong enough to make the morphology follow the substrate pattern, i.e., an A-rich quadratically perforated lamella (QPL) is formed that has no analogy in the bulk phase diagram. From this QPL structure in the vicinity of the substrate, necks emerge that reach the free top surface of the film, i.e., the upper half of the film also consists of a perforated B-rich lamellar sheet. The perforations, however, are disordered.

A more detailed analysis (see Figure 4) reveals that the short-ranged order of the necks reaching the top surface is predominantly hexagonal, while the long-ranged correlations have four-fold symmetry mirroring the influence of the underlying substrate pattern. Since both lamellar sheets are perforated the symmetric thin film morphology is bicontinuous. If we increase the film thickness, another perforated A-rich lamellar sheet will form and

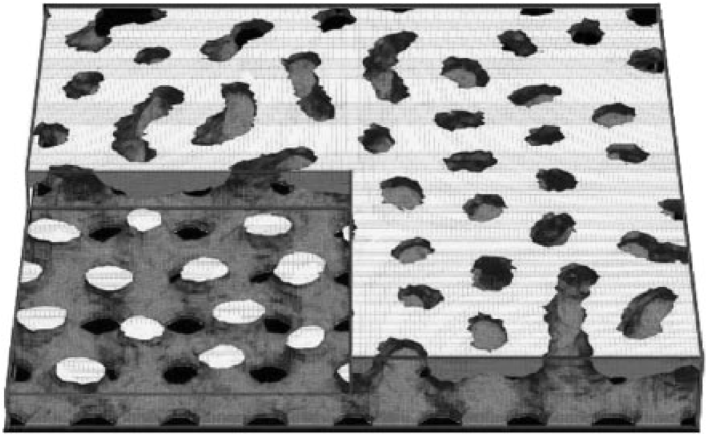

Figure 3.
Morphology of a thin film of diblock copolymer material on a patterned substrate that consists of a square array of spots that are attractive to one component (B). For clarity domains of the other component (A) are only shown and the interface between domains. The near-substrate morphology replicates the substrate pattern, and a quadratically perforated lamellar sheet is formed. The upper half of the film consists of a randomly perforated B-rich sheet. From Ref. 3.

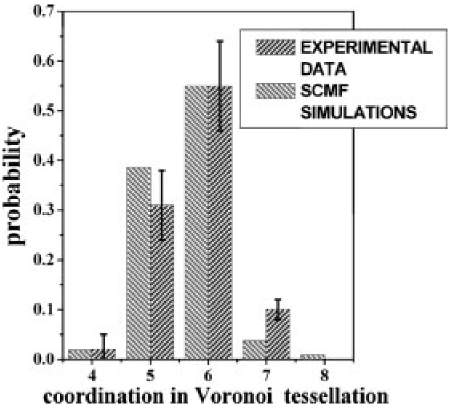

Figure 4.
Analysis of the short-ranged structure of the necks that emerge at the film's top surface by Voronoi tessellation. The graph shows the probability of neighbors of a Voronoi cell centered at the neck's position at the free, top surface. Both the analysis of SCMF simulations as well as of scanning electron micrographs of an experimental system are presented and quantitative agreement is found. The natural tendency of the necks to pack into a dense hexagonal structure competes with the influence of the square symmetry of the substrate pattern. On short distances the orientational correlations are predominantly six-fold, but the lack of symmetry between four- and seven-fold coordinated cells indicates the influence of the substrate pattern. From Ref. 3.

the morphology will remain bicontinuous. Such bicontinuous structures have been long searched for and they are only encountered in a small region of the bulk phase diagram of diblock copolymer materials (i.e., the microemulsion channel). Reconstruction of the soft morphology offers opportunities to fabricate these structures in symmetric systems without the need of fine-tuning the materials parameters (e.g., composition or molecular weight). Additionally, the channels on the side of the substrate perfectly register with the pattern thereby facilitating the connection of the bicontinuous, nano-porous material to external devices.

Concluding Remarks

We have discussed a particle-based simulation scheme – Single Chain in Mean Field Simulation – that combines aspects of field-theoretic calculations with simulation methods. Although the method is approximate, its underlying assumption – quasi instantaneous filed approximation – is controlled by a parameter that not only depends on the coarse-grained parameters of the physical system but also on the discretization of the numerical method. By a suitable choice of numerical parameters it is possible to accurately describe correlations and fluctuations that are ignored in self-consistent field calculations.[7] We have illustrated the ability to describe correlation effects by studying the intermolecular und intramolecular correlations in a melt of long homopolymers and compared the results of SCMF simulations to exact Monte Carlo simulations of the same model. Then we have discussed the application of SCMF simulations to explore the directed assembly of diblock copolymer materials in thin films on patterned substrates. SCMF simulations are particularly suited to investigate these systems because they allow to access large time and length scales, the coarse-grained model parameters can be directly related to experiments and yield a realistic description of the ordering kinetics in spatially inhomogeneous systems within the framework of the Rouse model.

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