MIT Open Access Articles

Communication: Lateral phase separation of mixed polymer brushes physisorbed on planar substrates

Massachusetts Institute of Technology

Communication: Lateral phase separation of mixed polymer brushes physisorbed on planar substrates

Reid C. Van Lehn and Alfredo Alexander-Katz

Additional information on J. Chem. Phys.

Communication: Lateral phase separation of mixed polymer brushes physisorbed on planar substrates

Reid C. Van Lehn and Alfredo Alexander-Katz
Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts 02139, USA

Here, we present a new method to model lateral phase separation in mixed polymer brushes physisorbed to a planar surface with mobile grafting points. The model is based on a local mean field theory that combines a Flory-Huggins approximation for interaction enthalpies with an Alexander-de Gennes brush entropy contribution. Using Monte Carlo sampling, the application of these two interactions to a lattice model yields a range of phase behavior consistent with previous theoretical and experimental work. This model will be useful for predicting mixed polymer brush morphologies on planar surfaces and in principle can be extended to other geometries (e.g., spheres) and polymer systems. © *2011 American Institute of Physics*. [doi:10.1063/1.3653937]

Polymer brushes are an important class of soft materials composed of polymers tethered to a surface. The grafting points may be fixed, as in the case of polymers covalently bound to the surface, or could be mobile, as in the case of physisorbed brushes. If the grafting density is sufficiently high, the tethered polymers will extend away from the surface to minimize steric overlap, forming the characteristic brush morphology.[1] When two (or more) polymer species are tethered to the same surface, the resulting system is referred to as a mixed polymer brush. The interaction between these two species, along with the interactions between each species and the solvent, gives rise to a range of possible surface morphologies. Depending on the difference in chain lengths, the mixed brush can undergo either lateral phase separation, where both species are exposed to solvent but develop ordered morphologies in the plane, or vertical phase separation, where a single species preferentially interacts with solvent while the other collapses near the surface. These morphologies also depend on structural factors including the tethering density, phase fraction of each species, molecular weight, and chain lengths of the polymers. Recently, there has been significant interest in predicting laterally phase-separated mixed polymer brush morphologies on planar substrates,[2–4] motivated by applications in protein adsorption,[5] drug delivery, and nanotemplating[6,7] and for the creation of stimuli-responsive systems.[8,9]

The behavior of polymer brushes has been studied in detail theoretically, beginning with the pioneering work of Alexander[10] and de Gennes[11] that resulted in an eponymous scaling theory for the free energy and height of the brush layer. Their scaling approach characterizes each polymer in the brush as a series of blobs with a uniform size determined by the confinement of surrounding chains.[12] This confinement and the influence of the good solvent leads the chains to strongly stretch away from the surface. The free energy of the brush is a function of the number of blobs, which are assumed to have an energy on the order of kT, and an elastic term characterizing this chain stretching. Beyond the Alexander-de Gennes model, polymer brushes have also been studied

using self-consistent field theory,[12–15] single-chain in mean-field theory,[16–18] molecular mean-field theory,[19] molecular dynamics simulations,[20] and Monte Carlo simulations.[21,22] Here, we present a novel model combining Flory-Huggins and Alexander-de Gennes theory to simulate the lateral phase separation of mixed polymer brushes with mobile grafting points. A strength of this method is computational efficiency– simulations complete in only a few minutes, enabling the creation of detailed phase diagrams to help predict equilibrium morphologies.

We consider a system composed of two polymer species grafted to a planar surface at a density in the brush regime and exposed to a non-selective good solvent. The polymers are allowed to rearrange across the surface to minimize the system free energy. The two species are assumed to have different chain lengths leading to the formation of two brush layers. The first layer is uniformly thick and consists of all the "short" polymer chains and part of the "long" polymer chains, while the second layer is formed from the ends of the long polymers that extend farther into the solvent. In both layers, strong stretching consistent with the Alexander-de Gennes approach is assumed. Figure 1 illustrates a schematic drawing of the system. This system is interesting because there is a competition between the entropy of mixing of the two species due the mobility of grafting points, enthalpic Flory-Huggins interactions, and the entropic/elastic contribution arising from strong stretching of the longer chains. This competition gives rise to rich phase behavior, including the possible formation of mixed, macrophase separated, and microphase separated states at large values of the enthalpic parameter where macrophase separation alone would typically be expected.

The first interaction considered in the model is a pair-potential for the enthalpic interaction between chain i and neighboring chains:

$$U_i^{F-H} = kT\chi \sum_{j \in n(i)} b_{ij}, \qquad (1)$$

$$b_{ij} = \begin{cases} 0 & \text{if } i, j \text{ both short or both long} \\ 1 & \text{if } i, j \text{ are different.} \end{cases}$$
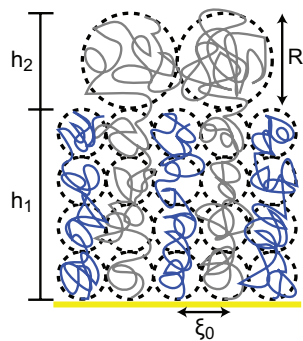
FIG. 1. Illustration of the mixed brush system consisting of short polymer chains with N_S segments each and long polymer chains with N_L segments. Both the long (gray) and short (blue) polymers are drawn as a series of blobs consistent with the Alexander-de Gennes approach. The polymers are tethered to the surface with a fixed grafting length ξ_0 that sets the lateral length scale. The radius of blobs in the upper brush layer, R, depends on the local volume fraction of long polymers ϕ around each chain. The height of each layer is denoted as h_1 and h_2, respectively.

Here, $n(i)$ is the set of nearest neighbors for chain i, reflecting the assumption of densely grafted polymers that only interact with a small subset of surrounding chains. The key parameter is χ, which is typically positive and can be interpreted as the degree of miscibility between the two polymer species. This χ parameter can be thought of as qualitatively and effectively similar to χN, the Flory-Huggins miscibility parameter commonly used to describe polymer blends.[23] Here, we drop the parameter N to maintain generality.

The second interaction is a mean field, many-body interaction to model the free energy of chain overlap between long polymer ends in the second brush layer. This "blob" interaction depends on the local density of long polymers which determines the size and number of blobs in the brush and thus the free energy. To calculate an approximate form for this interaction, we use equations originally derived by Komura and Safran[24] which in turn follow from the Alexander-de Gennes model. It is assumed that the long polymer ends are dense enough to overlap and can be described as a series of blobs. The size of the blobs, R_i, for chain i is related to the local density ϕ_i of long polymer ends around the chain and the grafting length in the bottom layer ξ_0 by $R_i(\phi_i) = \xi_0/\phi_i^{1/2}$. The free energy of the brush layer is proportional to the number of blobs in the system, which from geometry is h_2/R_i, where h_2 is the height of the second brush layer. Finally, h_2 is also a function of the number of statistical segments of the short polymer N_S and long polymer N_L, the grafting length ξ_0, the segment length of the polymer chain a, and a solvent quality scaling exponent ν. The lateral length scale is set by the grafting length ξ_0, since this parameter both affects the size of the blobs and sets a length scale for nearest neighbor enthalpic interactions. A detailed derivation is given by Komura and Safran with a final result of

$$U_i^{blob}(\phi_i) \approx kT \frac{h_2}{R} \approx kT(N_L - N_S)a^{1/\nu}\xi_0^{-1/\nu}\phi_i^{1/2\nu}$$

$$\approx kT\kappa\phi_i^{1/2\nu}, \qquad (2)$$

where $\kappa = (N_L - N_S)a^{1/\nu}\xi_0^{-1/\nu}$ is a dimensionless parameter combining all spatially uniform parameters. In the orig-

inal work by Komura and Safran, it was assumed that the surface coverage was uniform and thus ϕ_i was identical for each chain i in the second brush layer. However, by allowing ϕ_i to vary for each i, ϕ_i instead reflects the *local* confinement of each long polymer chain and depends on the morphology of the surface. The competition between enthalpic interactions between the short and long polymers, blob interactions between long polymers with each other, and the mixing entropy of the system thus gives rise to a range of lateral morphologies.

Monte Carlo simulations were used to find equilibrium system morphologies based on these two interactions. To simplify the calculations, the polymers were assumed to be tethered to a hexagonally close-packed lattice such that every lattice point represented either a long or short polymer.[25] The distance between lattice points was again given by the grafting length ξ_0. For each Monte Carlo time step, two neighboring lattice points containing polymers of opposite type were selected and the change in system energy for switching their positions was calculated. Following the Metropolis algorithm, the switch was accepted with a probability of,

$$P_{12} = \min(1, e^{-\Delta U_{12}/kT}), \qquad (3)$$

where $\Delta U_{12} = \Delta U_{12}^{F-H} + \Delta U_{12}^{blob}$ is the change in the total energy of the system for switching the positions of chains 1 and 2. Due to the lattice simplification, Eq. (1) was applied directly to calculate U_i^{F-H} for each chain $i = 1$ and $i = 2$ in their positions before and after the proposed switch, where the set of near-neighbors for each was defined by the lattice. To calculate $U_i^{blob}(\phi_i)$, we invoked a mean-field approximation where the phase fraction ϕ_i was given by the average density of *long* polymer chains around i, if i itself was a long polymer. In the lattice approximation, the average density was the fraction of sites occupied by long chains among the second nearest neighbor sites of chain i. Short polymers were ignored in the calculation of the blob energy change because the density of polymers in the first brush layer was uniform.

Each simulation was run for 200 000 time steps per site on a lattice with 1600 points and periodic boundary conditions. The initial state of the lattice was generated by randomly determining whether each site was a long or short chain, subject to the constraint of a fixed overall phase fraction f of long chains. Because each Monte Carlo step involved switching the polymer type on adjacent sites but not changing the relative proportion of each type, f was conserved throughout each simulation. There was no restriction on chain positions in the system, such that the initial random configuration had no bearing on the final morphology and macrophase separation was allowed. While previous simulation studies have assumed irreversible grafting that may limit the ability of the system to phase separate,[4,18,22] the assumption of unrestricted polymer rearrangement is appropriate for the formation of brushes by physisorption.[7]

A simulation for a single set of parameters finished in ~10 min using a single core of an Intel Xeon E5430 processor. Given this fast runtime, phase diagrams were generated using the results of over 6000 simulations each to define accurate phase boundaries. The heat capacity of the system was obtained from measuring energy fluctuations, with a peak
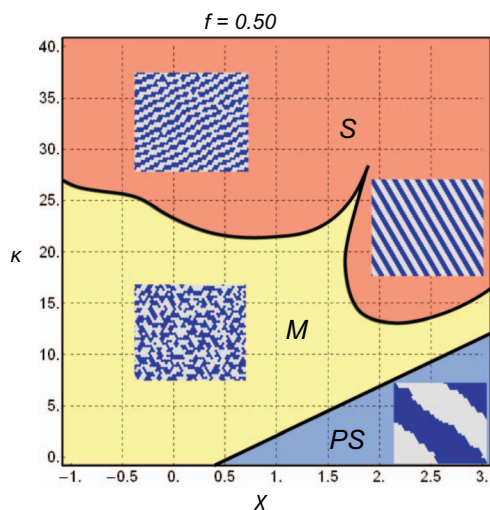
FIG. 2. Phase diagram for a phase fraction $f = 0.50$ of the mixed brush system as a function of κ, the dimensionless constant for the blob interaction, and χ, the Flory-Huggins interaction parameter. Thick black lines mark phase transitions. Three morphologies are observed—mixed (M), phase separated (PS), and striped (S). Simulation snapshots of the corresponding phases are included with long polymers drawn in gray and short in blue. Note that two simulation snapshots of the striped phase are shown, illustrating the well-aligned stripes observed for high values of χ.

FIG. 3. Phase diagram for $\chi = 1.5$ of the mixed brush system as a function of κ and f. Thick black lines mark phase transitions. Mixed (M), phase separated (PS), striped (S), and dimple (D) phases are observed. Simulation snapshots corresponding to the value of κ indicated by the dotted line are shown, illustrating the different observed phases as f is increased. Long polymer chains are drawn as gray and short chains are drawn as blue.

in the heat capacity indicating a phase transition.[26] Figure 2 shows a phase diagram and simulation snapshots of the system for a fixed phase fraction $f = 0.50$. Different phases are indicated as a function of the key parameters χ and κ from Eqs. (1) and (2). Phase transitions are indicated with black lines, with transitions identified by peaks in the heat capacity as well as visual inspection. All simulations were performed with $\nu = 3/5$ to represent a non-selective good solvent. In addition to typical cases where $\chi > 0$, the phase diagram additionally extends χ to negative values, representing polymers that are highly miscible due to hydrogen bonding, electrostatic, or other attractive interactions.[27]

The phase diagram successfully reproduces several established morphologies of polymer brush systems. A trivial example is $\kappa = 0$, implying that $N_L = N_S$ and there is no length difference between the two polymers in the system. In this case, the model correctly predicts phase separation (marked as PS in Fig. 2) if the value of χ is sufficiently positive to overcome the entropy of mixing, and complete mixing (M) for lower values of χ. For $\kappa > 0$, the blob interaction penalizes long polymers that are close together on the lattice, encouraging mixing and thus increasing the value of χ necessary for phase separation. As κ further increases, the system transitions into a striped, or ripple, phase (S) that has been previously reported in the literature.[3,28] Interestingly, this stripe morphology was itself tunable—at low values of χ, the stripes were largely disordered with noticeable defects, but as χ increased the enthalpic contribution from χ dominated over thermal fluctuations, leading to perfectly aligned stripes.

Figure 3 shows a phase diagram for fixed $\chi = 1.5$, while f and κ are allowed to vary. As in Fig. 2, phase separated (PS), mixed (M), and striped (S) phases are observed; however, for certain phase fractions an additional "dimple" phase (D) is
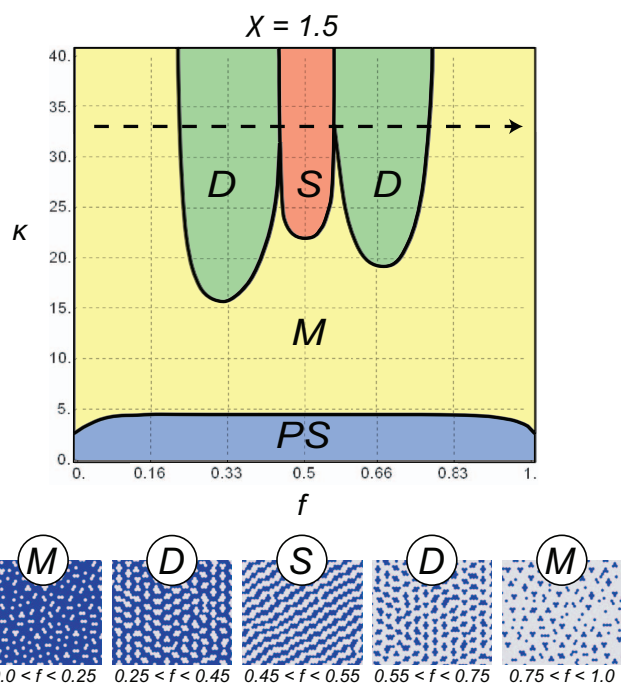
predicted. This phase consists of an ordered arrangement of clusters of the minority component surrounded by the majority component, and has also been previously identified in the literature.[2,3] Notably, the transition to the dimple phase as κ increases is asymmetric with respect to f, consistent with the application of the blob interaction to only long polymers in the model. The value of κ necessary to induce a phase transition is higher for larger values of f because the greater surface coverage of long polymer chains yields larger values of ϕ_i on average across the lattice. For a typical value in good solvent of $\nu = 3/5$, Eq. (2) shows that $U_i^{blob}(\phi_i) \propto \phi^{5/6}$, and hence changing the local density of long chains leads to a lower change in blob energy if ϕ_i is higher on average. The magnitude of the change ΔU_{12}^{blob} thus tends to be smaller than for higher values of f, requiring a greater value of κ for ordering to be thermodynamically preferred.

These phase diagrams show that a key tuning parameter to control phase behavior is κ. To put this parameter in some context, consider a system with $N_S = 200, N_L = 350, a = 1.0, \xi_0 = 3.0$, and $\nu = 3/5$, where a sets the length scale. Under these conditions, the radius of gyration R_G of the free short polymer is $R_G \approx 1/6 N_S^{3/5} a \approx 4.0$, which is greater than ξ_0 so that the system is in the brush regime.[1] Evaluating κ with these values from Eq. (2) gives a value of $\kappa \approx 24.0$. For this κ, the phase diagram in Fig. 2 predicts that if the amount of each polymer species is equal, a striped or disordered morphology can be obtained by modifying χ, with stripes preferred for most values of $\chi > 0$. Alternatively, the phase diagrams in Fig. 3 show that if χ is fixed at 1.5, the system can transition into a dimple morphology if the fraction of long polymer is

reduced below ≈0.45 or increased near ≈0.65. In principle, χ and κ can be tuned by chemical modification of the polymer chains, control of the grafting density, or choosing an appropriate chain length difference. This simple example illustrates the utility of the model in making quantitative predictions of use to experimentalists interested in self-assembling polymer brushes on surfaces with specific morphologies.

The results presented here demonstrate that combining the Flory-Huggins treatment of enthalpic interactions with an Alexander-de Gennes model for chain overlap is suitable for describing the lateral phase separation of mixed polymer brushes with mobile grafting points. The computational efficiency of the model enables the exploration of complex phase behavior and the generation of quantitative phase diagrams comprising thousands of simulation results. In principle, several modifications could be explored to further expand the model. For example, microphase separation of irreversibly grafted chains could be modeled by restricting the rearrangement of polymer chains to within a certain distance of their initial randomly generated configurations. Different grafting surface geometries (e.g., spheres) could be modeled by incorporating aspects of the Daoud-Cotton model[29] for spherical brushes. Given the generality of the model, it may also be used to model block copolymers or other tethered polymer systems that have been described by Alexander-de Gennes theory.[1] Finally, the comparison of the morphologies presented here and the emphasis on the length difference between polymers compares favorably with recent simulations of oligomers,[30–32] suggesting that the model may describe these systems as well. This future work could yield exciting new insight into morphological transitions in mixed polymer brushes and related systems, providing design guidelines for the nanoscale patterning of surfaces via self-assembly.

[1] A. Halperin, M. Tirrell, and T. P. Lodge, Adv. Polym. Sci. **100**, 31 (1992).

[2] M. Muller, Phys. Rev. E **65**, 030802 (2002).

[3] S. Minko, M. Muller, D. Usov, A. Scholl, C. Froeck, and M. Stamm, Phys. Rev. Lett. **88**, 035502 (2002).

[4] G. L. He, H. Merlitz, J. U. Sommer, and C. X. Wu, Macromolecules **42**, 7194 (2009).

[5] I. Szleifer, Biophys. J. **72**, 595 (1997).

[6] N. Ayres, Polym. Chem. **1**, 769 (2010).

[7] B. Zhao and W. J. Brittain, Prog. Polym. Sci. **25**, 677 (2000).

[8] B. Zhao and L. Zhu, Macromolecules **42**, 9369 (2009).

[9] M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, and S. Minko, Nature Mater. **9**, 101 (2010).

[10] S. Alexander, J. Phys (Paris) **38**, 977 (1977).

[11] P. G. de Gennes, Macromolecules **13**, 1069 (1980).

[12] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).

[13] S. T. Milner, T. A. Witten, and M. E. Cates, Macromolecules **21**, 2610 (1988).

[14] S. F. Edwards, Proc. Phys. Soc. London **85**, 613 (1965).

[15] G. H. Fredrickson, *The Equilibrium Theory of Inhomogeneous Polymers*, International Series of Monographs on Physics (Clarendon Press; Oxford University Press, Oxford, New York, 2006).

[16] M. A. Carignano and I. Szleifer, Macromolecules **28**, 3197 (1995).

[17] M. Muller, K. C. Daoulas, J. J. de Pablo, P. F. Nealey, and G. D. Smith, Soft Matter **2**, 573 (2006).

[18] J. F. Wang and M. Muller, J. Phys. Chem. B **113**, 11384 (2009).

[19] M. A. Carignano and I. Szleifer, J. Chem. Phys. **98**, 5006 (1993).

[20] D. I. Dimitrov, A. Milchev, and K. Binder, J. Chem. Phys. **127**, 084905 (2007).

[21] P. Y. Lai and K. Binder, J. Chem. Phys. **97**, 586 (1992).

[22] P. Y. Lai, J. Chem. Phys. **100**, 3351 (1994).

[23] P. J. Flory, *Principles of Polymer Chemistry*, The George Fisher Baker Nonresident Lectureship in Chemistry at Cornell University (Cornell University Press, Ithaca, 1953).

[24] S. Komura and S. A. Safran, Eur. Phys. J. E **5**, 337 (2001).

[25] Changing from a hexagonal to square lattice did not affect the phases observed in simulations, though the values of χ and κ corresponding to different phases were shifted due to the difference in the number of near-neighbors per lattice site. Simulation results were also not affected by an increase in system size.

[26] D. A. McQuarrie, *Statistical Mechanics* (University Science Books, Sausalito, California, 2000).

[27] I. K. Voets and F. A. M. Leermakers, Phys. Rev. E **78**, 061801 (2008).

[28] J. F. Marko and T. A. Witten, Phys. Rev. Lett. **66**, 1541 (1991).

[29] M. Daoud and J. P. Cotton, J. Phys (Paris) **43**, 531 (1982).

[30] P. K. Ghorai and S. C. Glotzer, J. Phys. Chem. C **114**, 19182 (2010).

[31] C. Singh, P. K. Ghorai, M. A. Horsch, A. M. Jackson, R. G. Larson, F. Stellacci, and S. C. Glotzer, Phys. Rev. Lett. **99**, 226106 (2007).

[32] A. Santos, C. Singh, and S. C. Glotzer, Phys. Rev. E **81**, 011113 (2010).