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Surface Energies and Self-Assembly of Block Copolymers on Grafted Surfaces

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(Dated:)

We present a theoretical analysis of the self-assembly of diblock copolymers on surfaces grafted with random copolymers. Our results demonstrate that the surface energies of homopolymeric components on grafted surfaces differ from the corresponding values for self-assembled morphologies. Moreover, grafted random copolymers are shown to adapt their conformations in response to the morphology of the overlaying block copolymer film to create chemical inhomogeneities which modulate the interfacial interactions. Consequently, the surface energy differences between the different components on the grafted substrate does not serve as a useful measure to predict the stability of self-assembly of the diblock copolymer film.

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The self-assembly behavior of di- and multiblock copolymers under confinement has attracted significant attention [1, 2]. Among the different morphologies exhibited by confined block copolymers, *perpendicularly* aligned lamellar and cylindrical phases have constituted a focus of attention in the design of semiconductor materials. Not surprisingly, extensive modeling and simulation work has focused on delineating conditions which lead to such morphologies in di- and multiblock copolymer films. While early work used simple scaling-type theories [3], later research used direct numerical approaches and Monte Carlo simulations to model the self-assembly behavior of diblock copolymers [4, 5] bounded by homogeneous substrates. Using such techniques, they predicted that substrates displaying an energetic preference for one of the components tend to induce the formation of parallel aligned phases. In contrast, for a "neutral" substrate, i.e. one which exhibits an almost equal preference for both components, perpendicular alignment was shown to be preferred.

Many of the common substrates exhibit an energetic preference for one of the components, making it a challenge to obtain perpendicularly aligned structures. To overcome this, a number of strategies such as chemical patterning, electric fields, graphoepitaxy, etc. have been pursued [2]. Of interest to this letter is a popular strategy which uses polymer-grafted substrates to achieve the requisite "neutral" interactions. Such approaches were pioneered by Mansky *et al.*, who showed that the surface energies of polystyrene (PS) and polymethylmethacrylate (PMMA) homopolymers can be tuned by the use of a grafted layer of random copolymer P(S-r-MMA) with different chemical compositions of the monomers in the grafted chains. In this manner, they demonstrated that the grafted layers can furnish a neutral surface which is effective in creating perpendicularly aligned phases [6, 7]. Subsequent work has advanced this idea to other systems by using alternative strategies such as crosslinking agents and/or grafting chemistries [2].

While broadly there is agreement between the experimental observations and theoretical results, outstanding issues remain in comparing the self-assembly of block copolymers on grafted polymer layers to theoretical models pertaining to homogeneous, hard confining surfaces. Indeed, grafted layers are *soft substrates* which can potentially modulate their thicknesses and/or allow for interpenetration to accommodate the morphology of self-assembly. Moreover, there is an underlying assumption that the surface energies of A and B *homopolymers*, usually determined through contact angle measurements, suffice to characterize the influence of interfacial interactions upon the self-assembly of the AB block copolymer [6–8]. However, such an assumption ignores the fact that the conformations and the energetics of block copolymers near grafted surfaces will depend explicitly on the self-assembled morphologies themselves, and can in general be different from the characteristics of the homopolymers. Moreover, *multicomponent* polymer brushes (such as the case of random copolymers) may also create lateral and/or normal chemical inhomogeneities to modulate their surface energies in response to the block copolymer self-assembly – an effect not captured in the surface energetics of homopolymer films. Such considerations prompt the question whether it is reasonable to use homopolymer surface energies to predict the self-assembly of block copolymers on polymer-grafted surfaces.

In this letter, we confront the above issues by modeling the self-assembly of diblock copolymers with an explicit representation of grafted surfaces. For the chemistry of the grafted polymers, we chose random copolymers as a representative system since it exemplifies many of the issues raised above, and has also constituted an active area of focus in lithography applications. We use a numerical implementation of polymer self-consistent field theory (SCFT) [9], the details of which are presented more elaborately in the context of our previous work which considered the behavior of homopolymer films (A) on random copolymer (AB) brushes [10]. In brief, to represent the grafted random copolymers, we use a *quenched* ensemble of chains with statistically determined sequences [11]

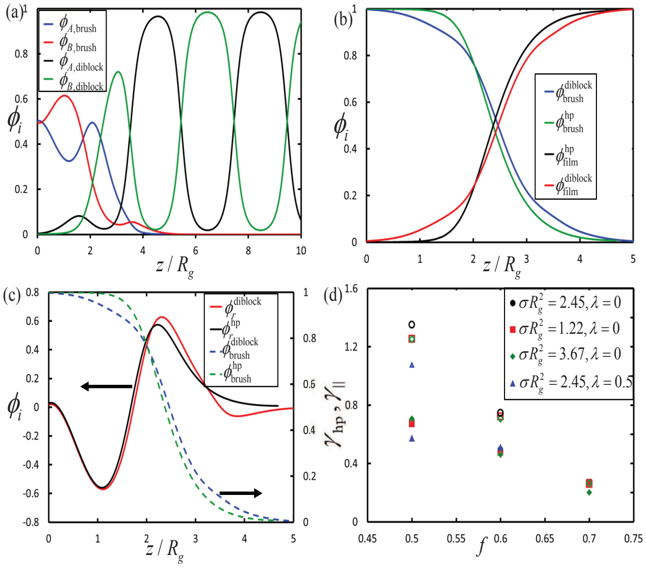

FIG. 1: In (a)-(c) parameters correspond to $\lambda = 0.9$, $\sigma R_g^2 = 2.45$ and $f_{brush} = 0.5$. (a) Composition profiles of different components of a diblock copolymer in parallel alignment on the grafted surface (z denotes the coordinate normal to the surface); (b) A comparison of the overall density profiles of brush and film components for homopolymer and diblock copolymer films; (c) A comparison of ϕ_r for homopolymer and diblock copolymer films. The brush volume fraction profile (secondary Y axis) is illustrated in dashed lines to highlight the interfacial zone; (d) Interfacial energies for a homopolymer film γ_{hp} (open symbols) and a diblock copolymer film $\gamma_{\parallel}$ (solid symbols) on brushes of different compositions f for different grafting densities σ and blockiness λ.

characterized by two parameters: f, which denotes the overall composition of species A in the random copolymer, and λ, which quantifies the "blockiness" or the tendency of a new segment to remain chemically equivalent to the previous one. Specifically, the limit $\lambda = 0$ corresponds to the purely random case and $\lambda = 1$ corresponds to a homopolymer with chemical identity determined by the probability associated with the first segment in the chain. We assume that the confinement has identical grafted layers on both surfaces and denote the grafting density as σ and report values normalized by the unperturbed radius of gyration of the grafted chains R_g. To isolate the specific effects of the random copolymers, we assume that the substrate on which the polymers are grafted is a "neutral" surface for the two components of the diblock copolymer. The results below are for a specified interaction between dissimilar segments (quantified by the Flory parameter χ, which we fix in the moderate segregation regime as $\chi N = 20$), and for the case when the number of segments in the grafted and the diblock copolymer are identical, and when the diblock copolymer is "symmetric" and forms lamellar phases. More details of the formalism and results for other parametric conditions will be presented in an expanded article.

Surface Energies of Homopolymer Films vs Self-Assembled Morphologies: In Fig. 1(a) we display results for the in-plane averaged composition profiles for parallel aligned diblock copolymers on symmetric random copolymer brushes ($f = 0.5$). We observe two striking features: (i) There is significant interpentration between the brush and the overlaying film, which manifests the "soft" nature of the grafted surface. The latter is clearly seen in the broad width of the interfacial zone between the brush and the film component in Fig. 1b; and (ii) There is a segregation of the brush components which leads to an enrichment of the A component (of the brush copolymer) in the interfacial zone between the brush and the overlaying film. The latter is evident in the enrichment function $\phi_r = \phi_{A,brush} - \phi_{B,brush}$ (normalized by respective volume fractions) displayed in Fig. 1c which is seen to become positive in the interfacial region. A similar enrichment was also seen in our previous work [10] which examined the behavior of homopolymer melts in contact with random copolymer brushes. In that situation, we showed that despite the symmetric nature of the brush ($f = 0.5$), the chain ends of the random copolymers can rearrange themselves in the interfacial zone to present an enriched amount of the component (in this case, A) chemically identical to the overlaying film. Such rearrangements were argued to reduce the enthalpic cost of contacts between the B component of the brush and the A component of the film.

In Figs. 1(b) and (c) we also compare the above morphological features with the corresponding results for a homopolymer film on an identical brush. While there are similarities between the behaviors of homopolymer and diblock copolymer films, quantitative differences are evident. Explicitly, we observe that the diblock copolymers exhibit larger interpenetration with the brush (evident in the larger overlap between the brush and film volume fraction profiles). Moreover, from Fig. 1c we observe that diblock copolymers induce a larger magnitude of "enrichment" of the brush component (the peak for the diblock film occurs at $\phi_r = 0.62$ whereas it occurs at $\phi_r = 0.54$ for the homopolymer case).

The above morphological differences are expected to prove crucial in comparing the surface free energies of the homopolymer and diblock copolymer filmes on grafted surfaces. Indeed, in our previous article [10], we demonstrated that the surface energies of polymers in contact with the random copolymer brush were correlated (inversely) to the magnitudes of the enrichment function ϕ_r. Moreover, prior studies have shown that the interpenetration widths between polymers and brushes are correlated (inversely) to the surface energies [12, 13]. In Fig. 1(d) we quantify these differences explicitly by comparing the surface energies of the parallel aligned lamella (for confinement thicknesses commensurate with the domain widths) with that of the homopolymer films. We observe that in all cases the parallel aligned lamella pos-

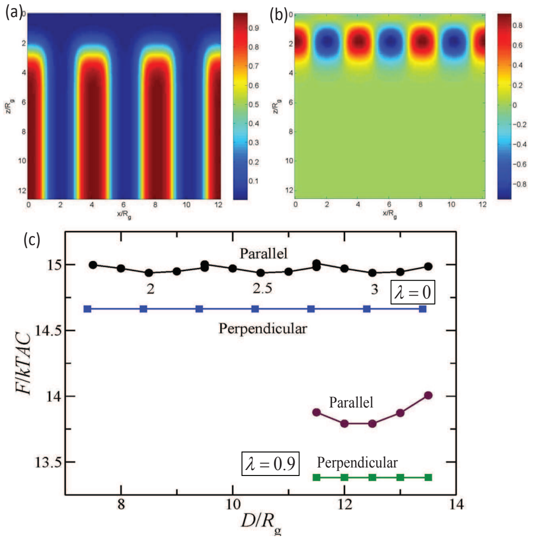

FIG. 2: In (a) and (b), the brush is grafted to the top surface and the parameters are the same as Figs. 1(a) - (c). (a) Composition profile of the A component of the diblock copolymers; (b) Enrichment function ϕ_r; (c) A comparison of the thickness dependent free energies (on a per chain basis) for parallel and perpendicular aligned lamellae (2, 2.5 and 3 denote the number of lamellae. For $\lambda = 0.9$ we display only the thickness region corresponding to 3 lamellae).

sesses smaller surface energies. Importantly, the results of Fig. 1c lead to the first conclusion of this letter that the surface energies of homopolymer films are not quantitatively the same as those for self-assembled morphologies.

Parallel vs Perpendicular Aligned Lamellae: In Figs. 2a-b we display the composition profiles and enrichment functions ϕ_r for the case where the diblock copolymer lamellae are aligned in a perpendicular manner. In Fig. 2b we observe a novel phenomenon in which the A and B components in the brush are seen to be enriched in the regions where they are in contact with the respective phases of the overlaying diblock copolymer. This behavior is a result of the perpendicular alignment of the lamellae and arises from the rearrangement of the brush chain ends so as to present an enriched phase of the appropriate component at the interface. While this phenomena is similar to that observed for parallel alignment, an intriguing aspect is the enhanced magnitudes of enrichment for perpendicular alignment. Explicitly, we observe that in the perpendicular alignment the magnitude of maximum in A (and B) enrichment in the interfacial region is 0.92, whereas it was 0.62 in the corresponding result for parallel lamellae (and 0.54 for the homopolymer case). We speculate that this enhanced enrichment (for perpendicular alignment) arises from a conformational rearrangement whereby grafted chains in the region in contact with the A portion of the block copolymer but whose ends are actually enriched in the B component *splay* towards the B portion of the block copolymer and contribute to the enrichment of B, and conversely, splaying of the A-rich chain ends from the region in contact with the B portion of the block copolymer enhances the enrichment of the A component [14]. Below, we demonstrate that this self-assembly driven adaptation of the brush has important consequences for the stability of different morphologies.

Our earlier discussion suggested that the surface energies of polymers on grafted surfaces are correlated to the enrichment function ϕ_r, and consequently we expect that the "enhanced" enrichment observed for the perpendicular lamellae would render the grafted surface to have *lower surface energies for such morphologies.* These expectations are confirmed in the results displayed in Fig. 2c which compares the thickness dependence of the free energies of the parallel and perpendicular alignments for brushes of different blockiness. The case displayed is for $f = 0.5$ which constitutes a symmetric brush and is expected to be a "neutral" surface for the block copolymer. For such a case, theoretical studies [4] have indicated that the perpendicular morphology is stable, but only due to small free energy differences arising from line tension effects at the interface between the lamellae and the surface [15]. In contrast, we observe that due to the enhanced rearrangement discussed above, the perpendicular morphologies on grafted random copolymer surfaces are significantly more stable compared to the parallel lamellae.

Another result evident in Fig. 2c in comparing grafted copolymers of different blockiness ($\lambda = 0$ and $\lambda = 0.9$) is that with larger blockiness leads to lower free energies for both the parallel and perpendicular alignments as well as an enhanced stability for the perpendicular alignment (i.e., $\lambda = 0.9$ has a larger free energy difference between the parallel and perpendicular alignments). These results are consistent with the fact that increasing blockiness leads to brush chains which have longer sequences of A or B monomers. Therefore, chain rearrangements can lead to more substantial enrichment at the interface and more favorable surface energies between the substrates and the block copolymers, and consequentlyresults in lower free energies for both the parallel and perpendicular morphologies. For the same reason, splaying of the chains is also expected to have a more pronounced effect for $\lambda = 0.9$, leading to an enhanced interfacial enrichment for perpendicular morphologies, rendering them more stable relative to the parallel alignment.

We note that the results for the two situations ($\lambda = 0$ and $\lambda = 0.9$) depicted in Fig. 2c are nontrivial, since they both correspond to symmetric brushes ($f = 0.5$) which constitutes a neutral surface for which there are no differences between the surface energies for the A and B homopolymer components. Since the free energies of the different morphologies and their stabilities differ between the two systems, the results already suggest that the relative surface energies of the homopolymeric components may not serve as a useful measure to determine

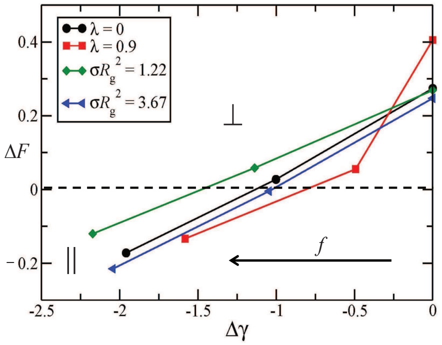

FIG. 3: ΔF and $\Delta\gamma$ for different grafting densities σ and blockiness λ. Different σs correspond to $\lambda = 0$, and different λs are for $\sigma R_g^2 = 2.45$. The different points for each parametric condition correspond to brushes with $f = 0.5, 0.6$ and 0.7 (representing increasingly A-rich random copolymers). $\perp$ and $\|$ denote regions of stability for the respective aligments.

the stabilities of different morphologies. To develop these considerations more quantitatively, we consider the quantity $\Delta\gamma$ defined as $\Delta\gamma = \gamma_{AS} - \gamma_{BS}$, with γ_{AS} and γ_{BS} denoting the surface energies of A and B homopolymers with the random copolymer brush. The latter quantifies the relative preference of the substrate to either of the components and is usually the outcome of macroscopic surface energy measurements. To address if there is at all a correlation between $\Delta\gamma$ and the stability of different morphologies, in Fig. 3 we compare the results for $\Delta F = F_{\|} - F_{\perp}$ ($F_{\perp}$ and $F_{\|}$ denoting the free energies of perpendicular and parallel alignment with the latter determined for thicknesses commensurate with the domain spacing) with $\Delta\gamma$ for different parametric conditions of the grafted surface. We observe that there is an enhanced regime of stability for perpendicularly aligned lamella ($\Delta F > 0$) extending to significantly non-neutral surfaces ($\Delta\gamma < 0$). This "super-neutrality" behavior is a manifestation of the morphology-driven rearrangements of the grafted surfaces seen in Fig. 2b and discussed in the context of Fig. 2c. More importantly, it is seen that while there is a general correlation that smaller $|\Delta\gamma|$s lead to perpendicularly aligned lamella, the correspondence between the two quantities is not unique. Indeed, we observe conditions where a specified $\Delta\gamma$ may result in $\Delta F > 0$ (perpendicular morphologies being prefered) or $\Delta F < 0$ (parallel morphologies being prefered), indicating the differing stabilities of parallel and perpendicular alignment. These considerations confirm that the morphology-driven interfacial interactions endow nontrivial stability characteristics for the different phases which cannot be uniquely correlated to the surface energy values.

In summary, in this letter we presented a theoretical analysis of the self-assembly of diblock copolymers on surfaces grafted with random copolymers to demonstrate that: (i) Surface energies of the homopolymeric components on grafted surfaces differ in general from the corresponding values for the self-assembled morphologies on such surfaces; (ii) Multicomponent grafted polymers may adapt their conformations to accommodate the self-assembly and in that process modulate their interfacial interactions with the overlaying film; (iii) The surface energy differences between the different components and the brush substrate does not provide a quantitative means to evaluate the stability of the resulting self-assembled morphology. While the above results were for lamellar phases, we expect even richer behavior to manifest when other self-assembly morphologies and/or the behavior of multiblock copolymers are considered. From an experimental perspective, our results suggest caution in using surface energy measurements to draw conclusions regarding the stability and mechanisms of self-assembly on grafted substrates. From a theoretical perspective, our results indicate that self-assembly on grafted polymer substrates possesses several novel features not captured by modeling them as smooth, confining surfaces, and motivate consideration of similar models for a wider class of systems.

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[14] Verification of this hypothesis requires an explicit calculation of the two point propagator, which is numerically cumbersome. However, results for other brush lengths (not presented in the article), indicate that the rearrangement effect becomes more pronounced for larger chain lengths. The latter is consistent with the splay mechanism presented in the article.

[15] For a stronger segregation of $\chi N = 30.0$, the free energy differences between perpendicular morphology and parallel morphologies were predicted to be $\lesssim 0.1kT$ [5]