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Selective Adsorption of Heteropolymer onto Heterogeneous Surfaces: Interplay between Sequences and Surface Patterns

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ABSTRACT: Monte Carlo simulations are performed to study selective adsorption of heteropolymers on heterogeneous surfaces. We focus on how statistical correlation between sequence types and surface patterns affects critical adsorption points (CAP), the point that marks the transition of a polymer chain, in contact with a surface, from preferring a nonadsorbed state in bulk solution to an adsorbed state on the surface. A large difference in the CAP's of different sequence types over the same surface identifies a window of interaction energies where selectivity is maximized. Our results show that statistical random surfaces (i.e, neighboring surface sites have no statistical correlation) cannot differentiate among different heteropolymer sequences. Conversely, random heteropolymers cannot differentiate different surface types. However, when neighboring surface sites have statistical correlations, selective adsorption of different heteropolymers is observed.

I. Introduction

Selective molecular recognition underlies many biological processes. Living organisms rely on the ability of biomolecules to interact preferentially with target molecules among many closely related, but different, rival molecules.[1] One of ways to gain insight into molecular recognition is to examine the structural features of interfaces formed between biomolecules.[2] Such studies have led to a "lock and key" picture, where two molecules recognize each other if their shapes and interactions at the interface are largely complementary. Another way is to use generic models for proteins or surfaces and study general rules that underlie molecular recognition. Adsorption of simple, two-letter heteropolymers on heterogeneous surfaces has been used as a model system to shed light on molecular recognition.[3–8] Studies of such model systems are also of great importance for the design of smart surfaces/sensors that are capable of discriminating between different analytes and toxins for targeted separations. A practical example in the context of polymer separation is the analysis and separation of statistical copolymers according to composition and sequence distributions (i.e., statistically blocky vs statistically alternating copolymers).

Muthukumar[3] and later Chakraborty and co-workers[9–13] have used such a model to study pattern recognition, which is characterized by a transition from an initial weak adsorption without pattern registry to strong adsorption where heteropolymer chains adopt the few configurations that maximize attractive interactions. With dynamic Monte Carlo simulations, Golumbfskie et al.[12] have shown that statistically blocky chains favor statistically patchy surfaces and statistically alternating chains prefer statistically alternating surfaces, without being kinetically trapped on other surfaces. Their results, while illustrating the importance of statistical correlation between surface and sequence patterns during adsorption, have so far been limited to a few combinations of surface and chain statistics. Jayaraman et al.[14] recently reported a theoretical scheme to design surfaces capable of recognizing different sequence types. They have shown that selective adsorption of block copolymers and/or alternating copolymers can be achieved on the designed surfaces, but selectivity for chains between these two extremes is less successful. Bogner et al.[7] have studied how heteropolymers with compact structures (representing folded proteins) distinguish different surfaces. Behringer et al.[8] have recently used a model with two rigid heterogeneous surfaces and have shown that cooperativity between interacting sites, defined by statistical correlation, enhances selectivity.

In the current study, we wish to uncover the general rules that govern selective adsorption of heteropolymers over heterogeneous surfaces. In particular, we ask how the critical adsorption points (CAP) of different sequence types on different surface patterns depend on statistical correlations between sequences types and surface patterns. The critical adsorption point marks the transition of a polymer chain, in contact with a surface, from preferring a nonadsorbed state in bulk solution to an adsorbed state on the surface. Our hypothesis is that a large difference in the CAP of two different sequence types over the same surface identifies a window of conditions to which the surface interaction can be tuned such that only one type of sequence will be preferentially adsorbed, hence obtaining high selectivity. We will present results of Monte Carlo simulations that reveal the dependence of CAP's on the statistical correlation between sequence types and surface patterns. We will then show that selectivity of different sequences on a given surface is achieved for sequences having different values of CAP. Most interestingly, we show that statistical random surfaces (i.e, neighboring surface sites having no statistical correlation) cannot differentiate among different heteropolymer sequences. Conversely, random heteropolymers cannot differentiate among different surface types. However, when neighboring surface sites have statistical correlations, selective adsorption of different heteropolymers is observed.

II. Simulation Details

II.1. Models for Surfaces and Chain Sequences. In the current paper, heteropolymer chains are modeled as self-avoiding walks on a simple cubic lattice. The examined chain length N varies from 26 to 250, with $N = 100$ being the most studied. All chains are composed of 50% A monomers and 50% B monomers but have different sequence types. In the current study, we have examined both regular patterned sequences and statistical (AB) copolymers. The regular patterned sequences examined include $(A_1B_1)_{N/2}$, $(A_2B_2)_{N/4}$, $(A_3B_3)_{N/6}$, and $(A_4B_4)_{N/8}$ block copolymers and diblock copolymers. These sequences are specified manually in the simulations. The A_1B_1 type is also referred as a completely alternating copolymer. The statistical disordered copolymers do not have a specified sequence pattern,

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but their sequences can be characterized by the statistical correlation of the monomers in the chain sequence, by defining a parameter, λ, ranging from -1 to $+1$. $\lambda = P_{AA} + P_{BB} - 1$, where P_{XY} is the conditional probability of an X monomer immediately following a Y monomer.[13] According to this definition, for a completely alternating chain, P_{AA} and P_{BB} both equal zero and $\lambda = -1$; for a diblock copolymer, $P_{AA} = P_{BB} = 1$ and λ approaches $+1$. For any statistical copolymer, λ ranges from -1.0 to 1.0, depending on the values of P_{AA} and P_{BB}. If the identity of the *i*th monomer is independent of the previous $(i - 1)$th monomer, then $P_{AA} = P_{AB} = P_A$, where P_A and P_B would be the probability of finding A and B monomers along the chain, respectively. In this case $\lambda = 0$, and in the absence of higher neighbor correlations, we refer to the chain as a statistically random copolymer. However, if $P_{AA} > P_A$, then $\lambda > 0$; the chain tends to have blocks of A and B, and we refer the chain as being statistically blocky. Alternatively, $\lambda < 0$ are the statistically alternating chains. In the current study, we have restricted ourselves to the case $P_A = P_B = 0.5$. As a result, $P_{AB} = P_{BA}$ and $P_{AA} = P_{BB}$ when ignoring end effects. For statistical copolymers with λ values ranging in between -1 and $+1$, we have used a Monte Carlo algorithm to generate the desired sequence. The algorithm starts first by assigning the monomers on a chain as either A or B randomly but with a constraint that exactly 50% of monomers will be A or B, respectively. This first step generates chains with λ values that have a Gaussian distribution around $\lambda = 0$ (see data in our previous study).[15] Then a Monte Carlo search calls for a swap between two different monomers A and B, until P_{AA} and P_{BB} become close to acceptable values specified by $P_{AA} = P_{BB} = (\lambda + 1)/2$. The sequence thus generated with a given λ value is then used in subsequent simulations.

The heterogeneous surfaces considered are composed of 50% of type 1 and 50% of type 2 sites. There are no neutral sites (i.e., surface loading is 100%). The surface statistics are characterized by the order parameter, OP,[14] which is defined by $\mathrm{OP} = (\sum_{i=1}^{N}\sum_{j=1}^{z} s_i s_j)/zM$, where $z = 4$, the coordination number for a solid surface on a simple cubic lattice, M is the total number of surface sites, i and j are nearest-neighbor sites, and s is defined based on the surface site identity, with $s(\text{type 1}) = +1$ and $s(\text{type 2}) = -1$. The OP describes the patchiness of the surface and has a range identical to λ, with OP $= -1$ for an alternating surface, OP $= 0$ for a statistical random surface, and OP near $+1$ for a patchy surface. We note that a one-dimensional OP can be calculated to quantify chain statistics using the equation for OP shown above with $z = 2$ and M equal to the total number of beads in the chain. Except for small differences due to end effects, this 1D OP gives the same value as λ, confirming that λ is equivalent to one-dimensional order parameter. Therefore, the statistical copolymer chain and statistical disordered surface are said to have matching statistics if λ = OP. In this study, we have examined statistically disordered surfaces with different OP values as well as regular checkerboard surfaces including 1 × 1, 2 × 2, 3 × 3, and 4 × 4 checkerboards. The regular checkerboard surfaces are generated manually. The statistical disordered surfaces with different OP values are generated by simulating an Ising model with nearest-neighbor interaction. One disordered surface with a given value of OP is generated and is then used in subsequent simulations. Both surface patterns and sequences used are quenched in our simulations.

The statistical copolymer chain and statistical disordered surface are said to have matching statistics if λ = OP. We note that sequence order parameter, λ, is equivalent to a one-dimensional order parameter. Both λ and OP reflect nearest-neighbor correlation. If there is no nearest-neighbor correlation, then λ = OP = 0. However, for regularly patterned sequences like A_2B_2 and A_3B_3, the order parameter λ itself is not sufficient to characterize the sequence since the monomers now have second and higher neighbor correlation. The same can be said about the checkerboard surfaces.

Attractive interactions are applied when monomers occupy lattice sites adjacent to surfaces. Two monomer types and two surface site types are used, resulting in four possible interactions: ϵ_{A1}, ϵ_{A2}, ϵ_{B1}, and ϵ_{B2}. We consider only cases where $\epsilon_{A2} = \epsilon_{B1} = 0$, while $\epsilon_{A1} = \epsilon_{B2} = \epsilon_w > 0$, representing an attractive interaction. No other interactions are applied, and the units of all interactions are reduced by kT.

II.2. Determination of Critical Adsorption Point (CAP) via Biased Chain Insertion Method. To determine the critical adsorption point of a chain with a given sequence type on a given surface pattern, we first determine standard chemical potentials, μ^0_{surf} and μ^0_{bulk}, using the biased chain insertion method,[16] where μ^0_{surf} and μ^0_{bulk} are the standard chemical potentials of a chain attached to a surface and in bulk solution, respectively. The standard chemical potential of a chain is calculated from the ensemble average of the Rosenbluth−Rosenbluth weighting factor, $W(N)$, which is given by[16]

$$\beta\mu^0 = -\ln\langle W(N)\rangle = -\ln\left\langle \prod_{i=1}^{N} w_i \right\rangle \quad \text{and} \quad w_i = \frac{\sum_{j=1}^{z} \exp(-\beta E_j)}{z} \tag{1}$$

where z is the lattice coordination number ($z = 6$ for simple cubic lattice) and E_j is the energy of *i*th inserted monomer in the *j*th potential direction. Typically, the chemical potential is determined based on about 20 million copies of trial chain conformations generated with biased insertion. For the determination of μ^0_{bulk}, a chain is inserted randomly in a cubic box with periodic boundary conditions applied in all three directions. We typically have used a cubic box with 100 × 100 × 100 for the bulk solution. The exact size of the simulation box being used should not affect the values of μ^0_{bulk} determined as long as the box size is several times larger than the chain size, which is true for the chains studied here. For the determination of μ^0_{surf}, a chain is inserted into a tetragonal box of size 250 × 250 × 100 along the *x, y*, and *z* directions with a solid surface at the $z = 1$ plane that has a quenched surface pattern. The chain is inserted with at least one monomer, picked randomly along the chain, and placed randomly near the $z = 1$ surface (on the $z = 2$ layer). Note the surface pattern used here is quenched. The trial chain is inserted randomly over different surface regions; the ensemble average performed in eq 1 includes average over different surface regions for the surface with the given OP value. There is another solid surface at the $z = 100$ layer, but this surface does not play any role since it is kept far removed from the $z = 1$ plane. No segments of inserted chain attached to the surface can potentially make contacts with surface sites at $z = 100$ layer. The standard chemical potential difference, $\Delta\mu^0 = \mu^0_{\mathrm{surf}} - \mu^0_{\mathrm{bulk}}$, then leads to the parameter K_0, where $K_0 = \exp(-\beta\Delta\mu^0)$, which is analogous to a partition coefficient for a chain moving from a bulk solution to be adsorbed on a surface at infinite dilution. In general, the larger the K_0 is, the stronger the adsorption. The critical adsorption point (CAP) is determined according to the procedures described in our previous work.[15,17] Briefly, K_0 is determined for several values of ϵ_w for chain lengths N ranging from 25 to 250, and the standard deviation in K_0, $\sigma(K_0)$, for each value of ϵ_w over these chain lengths is calculated. The critical condition is found as the value of ϵ_w where $\sigma(K_0)$ is at a minimum, the point where K_0 becomes least dependent on chain length. More discussions on the how this point is related to the CAP can be found in our earlier work.[15]

II.3. Determination of Selectivity via Grand Canonical Monte Carlo Simulations. Additionally, we have also performed grand canonical Monte Carlo simulations (GCMC) to compare the adsorbed amount of given sequences on a given surface. For the convenience of simulation, we have used a slit pore where two surfaces with a given pattern or a given order parameter, separated by a distance D, form a pore region. The simulation box contains two surfaces in the $z = 1$ and $z = D + 1$ plane, where D is the slit width, and periodic boundary conditions were applied in the x and y directions. The two surfaces at $z = 1$ and $z = D + 1$ have the same surface statistics. The use of pore surfaces, instead of an open surface in direct contact with a bulk solution, not only provides a computational convenience but also is relevant to experiments where surfaces are provided by porous materials. Typical values of D used are 20−30, and the chain length studied in GCMC simulations is around 100. GCMC simulation then determines the concentration of chains inside the pore $\langle\phi_{in}\rangle$ at the given bulk concentration of $\langle\phi_b\rangle$. The details of how GCMC simulations are used to determine the partition coefficient K at a given bulk concentration $\langle\phi_b\rangle$ can be found in our earlier paper.[18] Basically, two GCMC simulations with the same chemical potential μ are performed: one in a box representing the bulk solution and one in a slit pore. Average concentrations $\langle\phi_b\rangle$ and $\langle\phi_{in}\rangle$ are obtained in the two simulations, and the partition coefficient $K = \langle\phi_{in}\rangle/\langle\phi_b\rangle$ is computed. Since in the current study there are no other pairwise interactions except for the surface/bead interactions, there will be no differences for different sequences in bulk solutions. In other words, at the given input of chemical potential, $\langle\phi_b\rangle$ for different sequences are the same. However, $\langle\phi_{in}\rangle$ will vary depending on the sequence types. After determining the partition coefficients for two different sequences in a given pore, we define a selectivity $S = K(\text{seq I})/K(\text{seq II})$, which reflects the selectivity of a given pore surface toward a specific sequence. If $S = 1$, then the surface shows no selectivity toward the two sequences; if $S > 1$, then sequence I is preferentially retained in the pore. We note that this selectivity S obtained does not include potential competition of two sequences toward the same surface since K(seq I) and K(seq II) are obtained separately. The selectivity thus determined is relevant to experiments when the two sequences do not have to compete for surface sites (i.e., when the surface adsorption is below the saturation limit). When both sequences may compete for the same surface sites, the selectivity could be higher than what we have obtained here. In the future, we will modify our GCMC simulations to determine the selectivity S when two or more sequences are present simultaneously and compare the selectivity obtained in the current study to delineate the effect of competition.

III. Results

III.1. Statistical Correlation on the Critical Adsorption Point. We first examine how the critical adsorption point (CAP) of statistical copolymers on a given type of surface may shift depending on the statistical correlation between the surface and copolymer chain sequences. Table 1 summarizes values of ϵ_w at the CAP for different polymer sequences on different surface types. In this section, we did not examine regularly patterned sequences except the completely alternating chains and diblock copolymers. All chains and surfaces in Table 1 have fixed chemical compositions; the only variation is in the distribution of the sites. Therefore, differences in the observed value of ϵ_w(CAP) reflect the effect of correlation between λ and OP. Also note that the sequence with the lowest value of ϵ_w(CAP) will be most susceptible to being adsorbed on the surface.

We first examine the data in Table 1 for an alternating surface (OP = −1). In this case, the alternating chain has the lowest value of ϵ_w(CAP), and ϵ_w(CAP) increases with the sequence order parameter, λ. Even in comparison with chains that are close to alternating ($\lambda = -0.75$), the alternating chain has a much lower ϵ_w(CAP). Figure 1a shows the values of K_0 against chain length, N, for sequences with several values of λ when $\epsilon_w = 0.28$. Clearly all other sequence types have much smaller K_0's than the alternating sequence type. Since the K_0 value is related to chromatographic retention time, these results suggest that an alternating surface, when placed in contact with a solution containing a mixture of copolymers with fixed chemical composition but different sequence types, will most likely take up chains with alternating sequences. Results above a highly patchy surface, with OP = +0.94, exhibit a similar correlation between λ and OP, with diblock copolymers being most susceptible to adsorption on the patchy surface (i.e., it has the lowest ϵ_w(CAP)), followed by statistically blocky chains with $\lambda = +0.84$.

Table 1. Critical Adsorption Points for Heteropolymer with Different Chain Sequence Types Adsorbing onto Heterogeneous Surfaces with Different Patterns

surface types with order parameter OP	sequence λ	ϵ_w at CAP
alternating surface, OP = −1	−1	0.28
	−0.75	0.4
	−0.5	0.44
	0.0	0.49
	+0.5	0.53
	+1	0.55
patchy surface, OP = +0.94	−1	0.55
	0	0.49
	+0.5	0.45
	+0.84	0.39
	+1	0.31
moderately alternating, OP = −0.5	−1	0.39
	−0.5	0.47
	0	0.49
	+1	0.53
moderately patchy, OP = +0.5	−1	0.52
	0	0.49
	+0.5	0.47
	+0.84	0.44
	+1	0.40
random surface, OP = 0.0	−1	0.49
	0	0.49
	+1	0.49

Next we examine the data in Table 1 on a statistical disordered surface with OP = −0.5. Here the completely alternating chain still has the lowest ϵ_w(CAP), rather than the statistical copolymer with $\lambda = -0.5$ that matches the surface order parameter. This surface is able to differentiate among different sequences types, but the range of ϵ_w(CAP) observed for different sequences type becomes smaller than that on a completely alternating surface or on a very patchy surface. Figure 1b is a plot of K_0 vs chain length N on this statistical disordered surface when $\epsilon_w = 0.47$. Clearly the completely alternating copolymer is most retained on this surface, followed by the sequence types with more negative λ values. Block copolymers are least retained on this surface. The next row in Table 1 for a disordered surface with OP = +0.5 shows similar results. Here the diblock copolymer has the lowest ϵ_w(CAP), rather than the statistical copolymer with $\lambda = +0.5$ that matches the surface order parameter. Finally, the random surface displayed no selectivity; random, alternating, diblock, and even homogeneous sequences (all A or all B monomers, see ref 15) all have ϵ_w(CAP) = 0.49. Conversely, we also see that the ϵ_w(CAP) for the statistical random sequence with $\lambda = 0$ remains the same on all types of surfaces, implying this sequence cannot differentiate different surfaces.

III.2. Selectivity of Different Sequences by Statistical Disordered Surfaces. To further validate the above conclusions, we present grand canonical Monte Carlo (GCMC) simulation

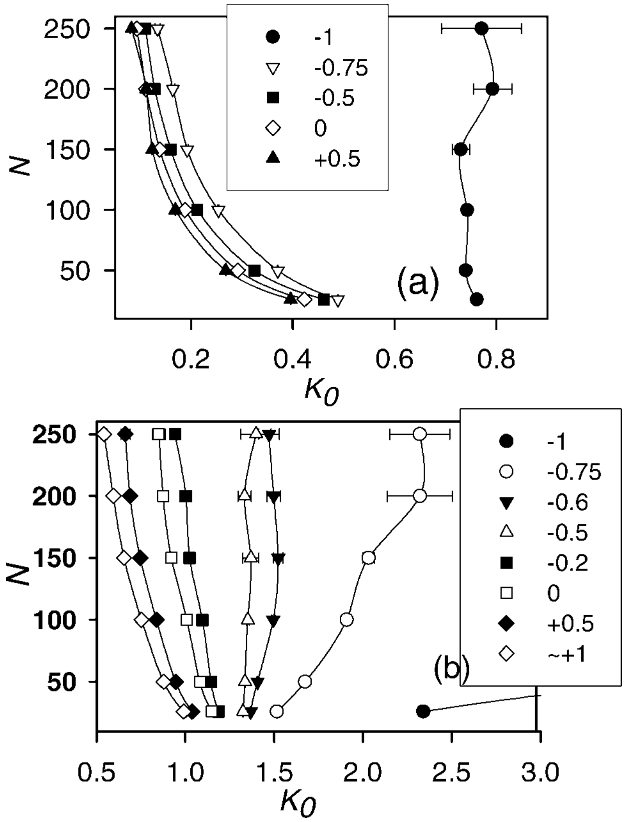

Figure 1. Adsorption of heteropolymer chains with different values of λ (given in figure legends) onto (a) an alternating surface (OP = -1) at $\epsilon_w = 0.28$ and (b) a moderately alternating surface (OP = -0.5) at $\epsilon_w = 0.47$. In (b) values of K_0 for $\lambda = -1$ are 3.6, 7.5, 13.9, 24.8, and 33.4 for $N = 50$, 100, 150, 200, and 250, respectively (data points are now shown). Error bars on estimated K_0 values when larger than the symbols are shown. We choose N as y-axis and K_0 as x-axis because of the convention used by experimentalists working in polymer separation.

results that allow for comparison of adsorbed amounts of different sequences on a given surface at a given bulk concentration ϕ_b. As state earlier, we have used a slit pore where two surfaces with the same given pattern (or same order parameter), separated by a distance D, form a pore region. Adsorption on a slit pore surface differs somewhat from adsorption on an open flat surface in direct contact with a bulk solution. For adsorption on slit pore surfaces, there is additional confinement effect on the adsorption, but the confinement effect can be gauged by the chain size relative to the pore size. When the confinement effect is weak, the adsorption in pore surfaces will approach the adsorption on an open surface in direct contact with the bulk solution. For the results reported here, we have used $D = 20$ or 30 and chains with a length $N = 100$, which has a radius of gyration in the bulk solution $R_{g0} = 6.6$, so D/R_{g0} ranges from 3 to 4.5, in a weak confinement regime. If the surface is nonadsorptive (i.e., $\epsilon_w < \epsilon_w$(CAP)), the chains are excluded from the pore surface so the partition coefficient $K = \langle\phi_{in}\rangle/\langle\phi_b\rangle$ is less than one. When the surface becomes adsorptive, then chains will be adsorbed on the two surfaces and form two adsorbed layers with a thickness about R_{g0}. We have checked numerically that once in the adsorptive regime most of the chains inside the pore are adsorbed on either one of the surfaces. Very few chains bridge the two surfaces or are not attached to the surfaces. The calculated concentration $\langle\phi_{in}\rangle$, however, counts the total concentration of chains inside the pore, which is computationally easy to determined within GCMC.

We have examined how the partition coefficient K for a given sequence varies with surface interaction ϵ_w changing from 0.0 to 2.0. Figure 2 shows the dependence of K(alternating), K(block), and $S = K$(block)/K(alternating) vs ϵ_w for chains with a length $N = 100$ partitioning from a bulk solution with a constant concentration $\phi_b = 0.012$ into a pore composed of a highly patchy surface with OP = +0.93. When $\epsilon_w \sim 0$, K remains low, less than one, for both sequences. When ϵ_w increases and approaches ϵ_w(CAP), K increases and becomes much larger than one. However, because the block copolymer has a lower ϵ_w(CAP) on the patchy surface than the alternating chains, we see that K(block) rises earlier than K(alternating), and this leads to a window of surface interaction where selectivity S is maximized. In this particular case, S is maximized at $\epsilon_w = -0.50 \pm 0.05$, above the ϵ_w(CAP) for diblocks but still below the ϵ_w(CAP) for alternating sequences. As ϵ_w increases further toward stronger segment−surface interaction, the selectivity of the pore decreases and seems to reach a plateau value. At $\epsilon_w = 2.0$, the interaction strength used in Jayaraman et al.[5] study, the selectivity $S \sim 1.66$, still larger than 1 but well below its maximum value ($S \sim 8$). Separation of two sequences by a given surface is best achieved when S is maximized. Therefore, results in Figure 2 suggest that studies on the selective adsorption of heterogeneous sequences by heterogeneous surface should focus on surface/segment interaction near the CAP, not at strong surface/segment interaction such as $2kT$. The results in Figure 2 also confirm that a difference in ϵ_w(CAP) for different sequences over a given surface opens up a window where the selectivity of a surface can be maximized. Conversely, when there is no difference in ϵ_w(CAP) for the two sequences, as for different sequences over the random surface, the plot of selectivity S vs ϵ_w is flat and S remains near 1.0 at all ϵ_w (data not shown). Clearly, selectivity of different sequences by a given surface is inherently related to the shift in ϵ_w(CAP) for different sequences.

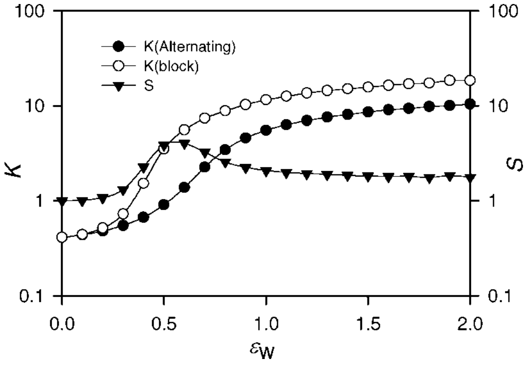

Figure 2. Plots of partition coefficient K for diblock (○) and alternating (●) chains partitioning into a pore with a highly patchy surface (OP = +0.94) at $\phi_b = 0.012$ as a function of ϵ_w. The selectivity, S, of diblock chains in reference to alternating chains, $S = K$(block)/K(alternating), is also shown. The surface forms a slit pore with dimension of 100 × 100 × 21 and the chain length $N = 100$.

Data in Table 1 suggest that on disordered surfaces with intermediate OP values the block copolymer will be most absorbed on a statistically patchy surface where as the completely alternating chain will be most adsorbed on the statistically alternating surface. We further confirm this by comparing the partitioning of chains with different λ values into slightly patchy pores with OP = +0.3. Indeed, the partition coefficient K for the block copolymer in the pores is always the largest compared with K for other sequence types. The selectivity for several chain sequence types in reference to a nearly random chain ($\lambda = +0.05$) partitioning into these pores at $\phi_b = 0.000\,89$ are shown in Figure 3. Even on these only slight patchy surfaces, selectivity is the largest for highly blocky chains and decreases as λ is varied from +1 to 0. The completely alternating chain, on other hand, is the least adsorbed on the patchy surface (i.e.,

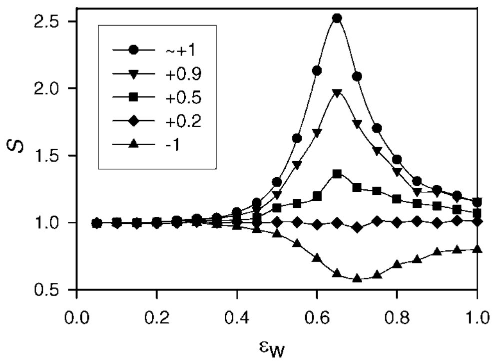

Figure 3. Plot of selectivity, S, against ϵ_w for statistical chains with the values of λ, given in the figure legend, in reference to a statistically random chain with $\lambda = +0.05$, partitioning into a slit pore composed of statistically patchy surfaces with OP = +0.3. The slit pore dimension used is 100 × 100 × 31, $\phi_b = 0.000\,89$, and chain length $N = 100$.

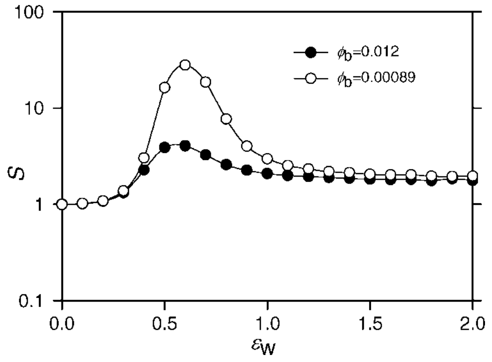

Figure 4. Plots of selectivity S of diblock chains in reference to alternating chains in a highly patchy pore at two bulk concentrations: $\phi_b = 0.012$ and $\phi_b = 0.000\,89$. The pore is the same as that used in Figure 2.

its $S < 1$). As the surface OP approaches zero and the surface becomes a statistical random surface, the selectivity toward any sequences is lost!

The bulk concentration ϕ_b also affects the selectivity significantly, especially near the condition where S is maximized. The selectivity is seen to continuously increase as ϕ_b decreases. Figure 4 compares the selectivity S of diblock chains in reference to the alternating chains in a highly patchy pore at two ϕ_b's. When ϕ_b is dropped from 0.012 to 0.000 89, the maxima of S increases from ~4 to ~28. The strong influence of bulk concentration on the selectivity is due to the strong adsorption of polymers on surfaces. When ϵ_w exceeds the ϵ_w(CAP) for a given sequence, the adsorption of that sequence on the surface is rampant while the K for the nonadsorbed sequence remains low. As a result, the lower the ϕ_b, the better the selectivity of that surface toward the adsorbing sequence.

III.3. Selectivity of Regularly Patterned Sequences on Checkerboard Surfaces. The above results show that a difference in the ϵ_w(CAP) for different sequences above a given surface is essential in order to achieve selective adsorption. It also shows that the sequence types on the two extreme ends of λ values, diblock chains with $\lambda = +1.0$ and completely alternating chains with $\lambda = -1.0$, will be most retained on statistical patchy and statistical alternating surfaces, respectively. Now we compare the adsorption of regularly patterned sequences on checkerboard surfaces. The sequences considered include A_1B_1, A_2B_2, A_3B_3, and A_4B_4, their λ values are −1.0, 0.0, 0.33, and 0.5, respectively, but these sequences are not statistically disordered sequences. Although A_2B_2 has $\lambda = 0.0$, it is certainly not a random copolymer, as there are second-order correlations (i.e., second-nearest neighbors are never the same bead type). The corresponding checkerboard surfaces considered are 1 × 1, 2 × 2, and 3 × 3 and 4 × 4, with the OP = −1.0, 0.0, 0.33, and 0.5, respectively. For each type of checkerboard surface, we also examine the adsorption of statistical disordered sequences with intermediate λ values. Here we have not examined the shift in ϵ_w(CAP) for different sequences but will compare the selectivity of different sequences directly. All selectivity S is defined in reference to a statistical random copolymer.

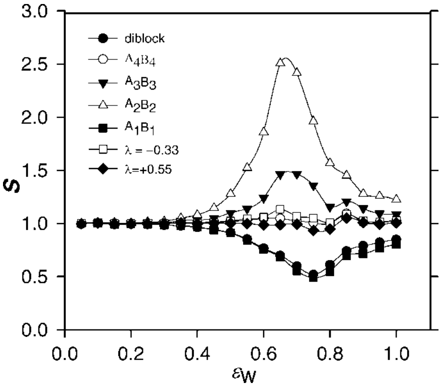

Figure 5. Plots of selectivity S for chains with different sequence patterns, specified by the legend, in reference to chains with a random sequence ($\lambda = 0.01$) partitioning into a slit channel with 2 × 2 checkerboard surface. The slit channel dimension is 100 × 100 × 21. The data for A_4B_4 sequence are masked by the data with $\lambda = -0.33$. Bulk concentrations of all sequences are at $\phi_b = 0.000\,89$.

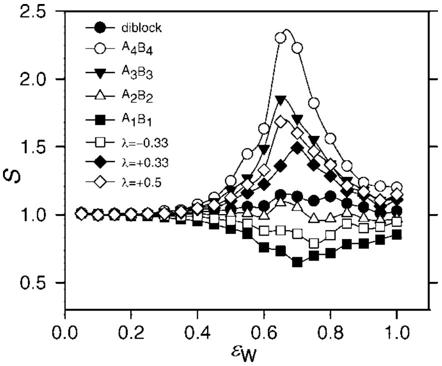

Figure 6. Plots of selectivity S for chains with different sequence patterns, specified by the legend, in reference to chains with a random sequence ($\lambda = 0.01$) partitioning into a slit channel with 3 × 3 checkerboard surface. The slit channel dimension is 100 × 100 × 21. Bulk concentrations of all sequences are at $\phi_b = 0.000\,89$.

Figure 5 plots the selectivity of various sequences, in reference to a statistical random sequence with $\lambda = 0.01$, on a 2 × 2 checkerboard surface. This surface is able to differentiate some sequences: the A_2B_2, A_3B_3, and diblock and alternating chains. Selectivity for other sequences remains near one within the error bars. Interestingly, on this 2 × 2 checkerboard surface (OP = 0), the A_2B_2 ($\lambda = 0$) chain is the most retained where the diblock ($\lambda = +1.0$) and alternating ($\lambda = -1.0$) chains are least retained. Note that while both the A_2B_2 and statistical random chains have $\lambda = 0$, the 2 × 2 checkerboard surface selectively adsorbs the A_2B_2 chains, indicating that agreement between OP and λ is not sufficient to explain the selectivity displayed for this surface. This could be expected since the surface now has a higher order correlation.

Figure 6 presents the selectivity of various sequences on a 3 × 3 checkerboard surface, which has OP = 0.33. On this surface, preferential adsorption of A_3B_3 over random sequence is observed, but the most retained sequence on the surface is

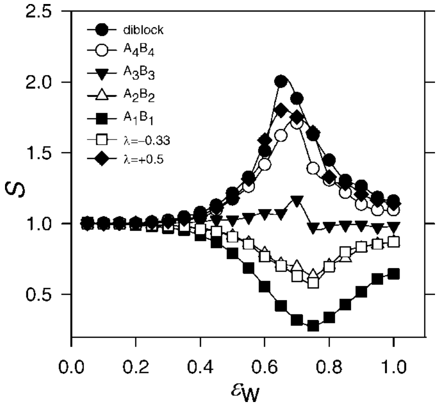

Figure 7. Plots of selectivity S for chains with different sequence patterns, specified by the legend, in reference to chains with a random sequence ($\lambda = 0.01$) partitioning into a slit channel with 4 × 4 checkerboard surface. The slit channel dimension is 100 × 100 × 21, and the bulk concentrations of the chains $\phi_b = 0.000\,89$.

A_4B_4, not A_3B_3. Statistically disordered sequences with $\lambda > 0$ are preferentially adsorbed on this surface compared to the random sequence. On the other hand, sequences with $\lambda < 0$ are less retained than the random sequences. For this surface, the correlation between λ and OP still plays a role but is not the only determinant. The 4 × 4 checkerboard surface has OP = 0.5. On this surface, the block copolymer becomes the most retained sequence, followed closely by A_4B_4 or statistical disordered sequence with $\lambda = 0.5$ (see Figure 7). On this surface, sequences with negative λ values are less retained than random sequences.

The results of these regularly patterned sequences on checkerboard surfaces reveal more complexity in the selective adsorption. The surface order parameter and sequence order parameter still play a role when their values are nonzero, but they are not the only factors that influence the selective adsorption. In the case of 2 × 2 checkerboard surface, OP = 0, but selective adsorption of A_2B_2 is achieved while completely blocky ($\lambda = +1.0$) and completely alternating chains ($\lambda = -1.0$) are least retained.

IV. Discussion and Conclusion

We now discuss the physical meaning of the results reported above. We note that results reported in the current study, whether the CAP values or the selectivity S, do not contain the effect of competing for the surface sites. The CAP value is determined by considering only a given sequence above the given surface. The selectivity S is calculated on the basis of adsorbed amounts on a surface when two sequences are present separately, not simultaneously. The selectivity thus determined is relevant to experiments when the two sequences do not have to compete for surface sites (i.e., when the surface adsorption is below the saturation limit). An understanding of selectivity in the absence of competitive adsorption is, we believe, the first step to understand the selectivity when competitive adsorption also plays a role.

The computational results reported in section III.1 show that statistical correlation between sequences and surface patterns will affect the CAP value. This phenomenon was observed in earlier computational studies by Bratko et al.[9] and theoretical studies by Polotsky et al.[19] Bratko et al. examined the adsorption of statistical copolymers on heterogeneous surfaces with Monte Carlo simulations. They examined adsorption statistics such as fraction of bound segments of a single chain near a surface. Two types of sequences, with $\lambda = +0.4$ and $\lambda = -0.4$, were considered in their study. The heterogeneous surfaces were simulated with surface sites that fluctuate according a statistic, $\sigma^2 \exp(-\kappa r)$, where σ is the surface loading (i.e., number of surface sites interact with the polymer segments) and κ is the correlation length between the sites separated by a distance r. The surface thus generated is statistically patchy. A slightly modified statistic was used for a statistically alternating surface. They then reported numerical results on the fraction of adsorbed segments, P, of the chain as a function the surface loading. As σ increases, the fraction of adsorbed segments P changes from a nearly zero value to a plateau value. This change in fraction of adsorbed segments reflects the transition of the chain from nonadsorbed to adsorbed states. Their data showed that this transition occurred earlier for sequence with $\lambda = +0.4$ than for sequence with $\lambda = -0.4$ on a patchy surface. The reverse was true on the statistically alternating surface. Their variation in surface loading σ could be compared with our variation of surface interaction ϵ_w at the given surface loading, although the two procedures were not exactly the same. If we disregard differences in the two procedures, then their results agree with what we have observed in section III.1. The CAP value of a statistical blocky chain on a statistically patchy surface is smaller than that of a statistically alternating chain. Hence, the observed transition exhibited by the fraction of adsorbed segments in their study for a blocky chain over a patchy surface would occur earlier than for a statistically alternating chain over a patchy surface.

Theoretically, Polotksy et al.[19] used an approximate variational method and derived an equation for the CAP for heteropolymers over heterogeneous surfaces. At the 50:50 composition considered here, their equation predicts that the CAP decreases if both the surface and the polymer are patchy (OP > 0) and blocky ($\lambda > 0$). Also, their equation predicts that if the surface is statistically random, there will be no shift in the CAP for different sequence types. Our results in Table 1 agree with their prediction qualitatively. Polotsky et al., however, have not considered statistically alternating surfaces and sequences.

A simple intuitive explanation can be given on why statistically blocky chains are more easily adsorbed on patchy surfaces than statistically alternating chains. The adsorption transition is determined by two opposing forces: the entropy loss when the chain is placed near the surface and the enthalpy gain when the polymer segments make favorable contacts with the surface sites. When the surface is patchy, surface sites of the same type are clustered together. Blocky chains consisting of blocks of segments of the same type can interact favorably with the patchy surface. On the other hand, statistically alternating chains contain less blocks of segments of the same type. When such chain is placed near the surface, one can envision that enthalpy gain will not be as large as in the case of blocky chains.

While qualitative features of the results reported here could be understood, a quantitative description of the results is difficult to develop. A somewhat surprising result observed here is that on moderately patchy surface the block copolymers are most retained rather than the chains with matching statistics. This phenomenon is reflected in both the CAP values shown in Table 1 and K_0 values shown in Figure 2b as well as the selectivity S presented in Figure 3. Our current understanding of this result is the following. First of all, for statistical disordered sequences and surfaces, both the length of blocks and size of surface domains have a broad distribution. Determination of size distribution of surface domains is a relatively more difficult task. We present in Figure 8 the distribution of block lengths for a chain with $N = 100$ with three different sequence statistics: $\lambda = -0.5$, $\lambda = 0.01$, and $\lambda = +0.5$. The distributions in Figure 8 are obtained by analyzing the block lengths observed in a single realization of a sequence with the specified λ value, except for $\lambda = +0.5$ where 10 realizations were used. Averaging the

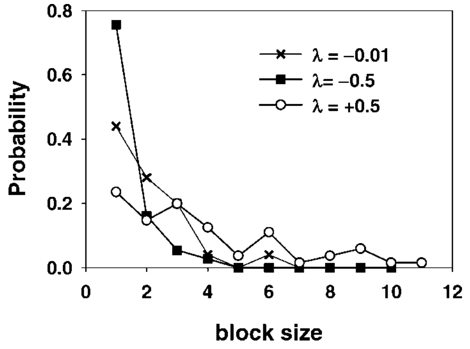

Figure 8. Block size distribution in a statistically disordered copolymer with three different statistics: $\lambda = -0.5$, $\lambda \sim 0.0$, and $\lambda = +0.5$. The distribution is obtained from a chain with length $N = 100$ with a single realization of the sequence except for the case of $\lambda = +0.5$ where 10 realizations of the sequence were averaged.

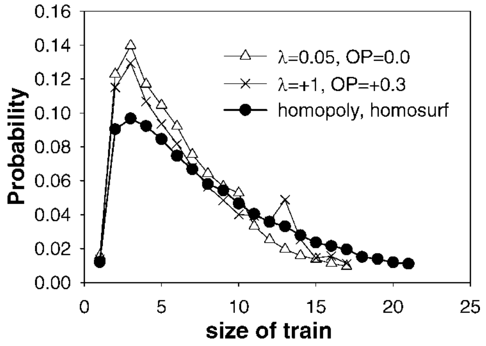

Figure 9. Probability of train size distribution observed in the adsorbed chains. All distributions were obtained at $\epsilon_w = 0.65$, $\phi_b = 0.000\ 89$, and chain length $N = 100$. Figure legends give the statistics of the chain and surface order parameter. The last set (●) is obtained for homopolymer chains adsorption on a homogeneous surface.

distribution over multiple copies of a given sequence type will lead to a smoother distribution curve. We have checked that the distributions actually are single-exponential decay functions. A statistically more blocky sequence with larger positive λ values tend to have a more broad distribution of block lengths (or a slower exponential decay function) rather than a distribution with a peak centered around a larger average block length. We conjectured that the size distribution of surface domains on statistically disordered surface would follow a similar exponential decay function. Now we examine the train size distribution of the adsorbed chain on the surface with $\epsilon_w = 0.65$, where the selectivity is maximized. A train is defined as a section of an adsorbed chain where all segments of that section are in contact with the surface. Figure 9 presents the train size distribution observed for homopolymer chains adsorbed over a homogeneous surface with $\epsilon_w = 0.65$, along with two such distributions obtained for statistical heteropolymer adsorption on heterogeneous surfaces. All three distributions have a similar shape. The most probable train size is around 3, and the distribution has a long tail that fits an exponential decay function. Because of such broad distributions observed both in terms of the block length, train size, and surface domain size, we believe that the selectivity achieved here is far from perfect registry made when the surface and chain sequences statistics match rather the selectivity arises from "fuzzy" match. We believe that the selectivity achieved here is of a different nature than the pattern recognition studied by Muthukumar and by Charkraborty and co-workers. Therefore, a perfect match between the two statistics—surface order parameter and sequence order parameter—may not result in the highest selectivity.

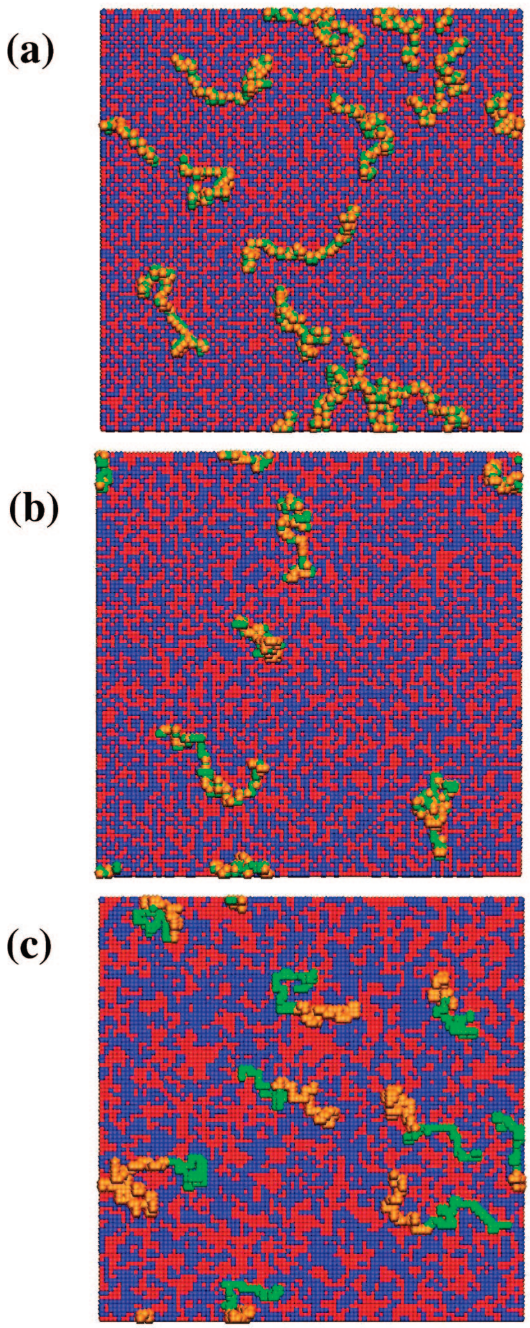

Figure 10. Representative snapshots generated via grand canonical Monte Carlo simulations of heteropolymers adsorption into heterogeneous slit surfaces. All three panels were obtained when $\epsilon_w = 0.65$ and a simulation box of 100 × 100 × 31 (only one surface with adsorbed chains are shown). The A beads shown in orange prefer the red surface sites, and the B beads shown in green prefer the blue surface sites. (a) Alternating chains adsorption on a statistical disordered surface with OP = −0.3. (b) A nearly statistical random copolymer ($\lambda = 0.05$) adsorption on a statistically random surface with OP = 0.0. (c) Diblock copolymer adsorption on a statistically disordered surface with OP = +0.3. Note the adsorbed chains are not lying completely flat on the surface.

Figure 10 present three configurations generated via GCMC simulations of heteropolymer adsorption on heterogeneous surfaces. On a statistically patchy surface with OP = +0.3, one can observe that the surface has domains that could accommodate the entire block of a diblock copolymer chain. This maybe the reason why our simulations show that diblock copolymer become the most retained one on moderate patchy surface. Figure 10a shows adsorption of alternating copolymers on a statistically alternating surface with OP = -0.3. The surface contained mostly alternating sites. That may be the reason that a strictly alternating chain become the most retained one on moderately alternating surface.

The results on adsorption of regularly patterned sequences on the checkerboard surfaces reveal more complexity in the rules governing the selective adsorption. For these polymers, the sequence order parameter λ itself is not sufficient to characterize the sequence pattern. Previously, Kriskin et al.[20] studied the adsorption of chains with block lengths of 4, 8, and 16 on a surface formed by stripes that were 8 surface sites wide and found that the chain with block length 16 was most readily adsorbed. This result is similar to our result on 3×3 and 4×4 checkerboard surfaces, in which A_4B_4 and diblock chain, respectively, were the most selected. However, on a 2×2 checkerboard, an A_2B_2 chain is most selected. At this stage, we cannot identify the rule governing the adsorption of the regular patterned sequences. However, these results combined with results for statistically disordered sequences point to one interesting feature: when the neighboring surface sites have no correlation such that the surface is a statistically disordered random surface (OP = 0), such surface has no selectivity for different sequence types. Conversely, statistically random heteropolymers where neighboring monomers have no correlation cannot distinguish different surface types. If we apply this observation to the molecular recognition process between biomolecules, our results then suggest that if interacting sites are distributed randomly on protein surfaces or on chains, molecular recognition is not possible. It is only when the distribution of interacting sites on surfaces is correlated that selective adsorption is possible. This therefore points to the importance of cooperativity of interacting sites for molecular recognition, a point that has been recognized in the study of biomolecular recognition.[2,8] However, our current conclusion is based on results limited to 50:50 composition with all interacting sites/monomers. We plan in the future to extend our investigation to nonequal composition with nonzero percentage of neutral noninteracting surface sites. The later should be a better mimic to real biological molecular systems. The results presented here may be important for the design of better nanosurfaces for biological recognition.

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