Solvent effects on heteropolymer adsorption and freezing

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Replica mean field theory is used to study the effect of solvent interactions on the adsorption of random heteropolymers onto heterogeneous surfaces. Random heteropolymers have been shown to undergo a pattern-matching adsorption transition, typified by a sharp transition from weak to strong adsorption on specific heterogeneous surfaces. It is found that polymers with higher excluded volume (good solvent) require higher surface site loadings to undergo the sharp adsorption transition. Furthermore, the final adsorbed polymer fraction is lower for high excluded volume polymers. This information can be used, for example, to design tailor-made membranes that prevent or allow for specific interactions with such protein-like molecules. Studies have shown that solution conditions often play an important role in determining the fouling of membranes by proteins. The results presented in this work may be important in directing applications involving the undesirable adsorption of proteins and other macromolecules that lead to the irreversible fouling of membranes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1368400]

I. INTRODUCTION

Discrimination between materials through molecule-specific binding is a concept encountered in many natural systems and used in many applications. For example, a relatively new area of research involves the development of synthetic molecular templates that can recognize specific molecules, based on the lock-and-key analogy (see Ref. 1 for a review). In addition, the recognition phenomena has been studied in the context of various applications such as viral inhibition[2,3] and chromatography for protein-specific separations.[4–6] On the other hand, recognition concepts that involve the selective binding and adsorption of molecules can be used to *moderate* their adsorption behavior, as in the case of protein fouling of membranes.

Random heteropolymers (RHPs), a class of polymers bearing a statistically random distribution of the different monomer units, have been the subject of many studies in recent years, especially as simple models to learn from the behavior of complex biomolecules.[7] However, unlike RHPs, coarse-grained models of proteins show a disordered (but *not* random) sequence distribution of the different amino acid units. Nevertheless, in analogy to proteins, the phase behavior of RHPs shows the existence of frozen phases where only a small fraction of the polymer's conformation space is sampled. Furthermore, RHPs have shown the ability to discriminate between patterned surfaces.[8–11]

This paper examines the effects of the solvent on the adsorption behavior of random heteropolymers, with relevance to protein deposition and fouling on membranes. In general, adsorption depends on the combination of the properties of the solid material, solute properties, and the interaction between the two. The interactions, in turn, are affected by the properties (chemical composition) and conditions (pH, temperature, pressure, etc.) of the solvent. The solvent mediates between the different interactions and therefore may play an important role in determining the adsorption

behavior of the macromolecules. For example, the amount of protein deposition on ultrafiltration membranes has been found to be largely affected by the solution conditions.[12–15] Therefore, understanding both the interactions of the polymers with the adsorbing media and with the solvent is crucial for practical system design.

Field theoretic methods are used to explore the effects of solvent interactions on the adsorption and freezing behavior of random heteropolymers. The replica field theoretic model developed is an extension of the model developed by Srebnik *et al.*[8] to study a system consisting of an infinitely dilute solution of RHPs in an ideal solution (theta solvent conditions) in the presence of a surface functionalized with a distribution of interacting sites. In this paper, the polymer–solvent interactions are implicitly taken into account through excluded volume interactions of the polymer segments. The physical system is depicted in Fig. 1. The polymer–surface interactions implicitly account for the mediation of the solvent as well. The solvent affects the interactions of the polymer with the surface in two ways: it provides a screen that intensifies or diminished these interactions and it influences the polymer entropy, both of which act to reduce or increase the free energy barrier of adsorption, depending on the solvent type. The effects of these interactions on the adsorption/freezing transition are discussed.

In the following section we present the physical model and the mean-field calculations. The results and their implications towards protein fouling of membranes are discussed in Sec. III. Concluding remarks are given in Sec. IV.

II. PHYSICAL MODEL

The adsorption of random heteropolymers made up of N monomers interacting with a multifunctional two-dimensional surface is modeled. The Hamiltonian of such a system, depicted in Fig. 1, subject to excluded volume interactions, v_0 (dependent on solvent and solution conditions), can be written as

$$-\beta H[\mathbf{r}(n),\theta(n)] = -\frac{3}{2l}\int_0^N dn\left(\frac{\partial \mathbf{r}}{\partial n}\right)^2$$

$$-\frac{v_0}{2}\int_0^N dn\int_0^N dn'\,\delta[\mathbf{r}(n)-\mathbf{r}(n')]$$

$$-\int_0^N dn\int d\mathbf{r}\,\kappa(\mathbf{r})\delta[\mathbf{r}(n)-\mathbf{r}]$$

$$\times\delta(z)\theta(n),\tag{1}$$

where n is a continuous index describing the contour location of the nth segment along the chain backbone. The location of the nth segment in three-dimensional space (from some reference point) is measured by the vector $\mathbf{r}(n)$. An Ising-type variable, $\theta(n)$, is used to specify the identity of the nth segment. For instance, $\theta(n)=\pm 1$ for a copolymer. $\theta(n)$ can also be a continuous function having a Gaussian distribution of segment interaction strengths. In this case, $\theta(n)$ fluctuates about a mean equal to $(2f-1)$, with f being the fraction of one monomer type. It is easy to show that when there are no chemical correlations along the chain the variance in the fluctuations in $\theta(n)$, $\sigma_2^2=\langle(\delta\theta(n))^2\rangle$, is equal to $4f(1-f)$.

The first term in Eq. (1) accounts for chain connectivity, with l being the Kuhn segment length of the polymer. The second term defines the polymer excluded volume interactions, of magnitude v_0. An ideal solution corresponds to $v_0=0$ and was treated in Ref. 8. The last term in Eq. (1) accounts for specific interactions with the surface, $\kappa(\mathbf{r})$, that depend on both the polymer segment type and the location on the surface. The fluctuations in the surface are described by a Gaussian process with short-ranged correlations and with variance $\sigma_1^2=\langle(\beta u)^2\rangle$, proportional to the loading of interacting sites, where u denotes the local segment-surface potential.

The partition function for a given realization of surface and sequence disorders is obtained by performing a thermal average over chain conformations,

$$G[\kappa(\mathbf{r});\theta(n)] = \int\int D\mathbf{r}(n)\exp\{-\beta H[\mathbf{r}(n)];\kappa(\mathbf{r});\theta(n)\}.\tag{2}$$

The free energy is calculated by averaging over the various realizations of the surface site and polymer segment disorders. The former average can be easily carried out assuming that the partition function is self-averaging with respect to $\kappa(\mathbf{r})$.[16–20] However, the partition function is not self-averaging with respect to the sequence disorder, and replica methods are used to perform the average over $\theta(n)$.[21–24] Carrying out the annealed average over $\kappa(\mathbf{r})$ and the quenched average over $\theta(n)$ (with $f=1/2$) results in the following m-replica partition function:

$$\langle G^m\rangle_{\kappa,\theta} = \prod_{\alpha=1}^m\int\int D\mathbf{r}_\alpha(n)\int\int D\kappa_\alpha(\mathbf{r})\exp\left\{-\sum_{\alpha=1}^m\left(\frac{3}{2l}\int_0^N dn\left(\frac{\partial\mathbf{r}_\alpha}{\partial n}\right)^2+\frac{v_0}{2}\int d\mathbf{r}\rho_\alpha^2(\mathbf{r})\right)\right\}$$

$$\times\exp\left\{-\frac{1}{2\sigma_1^2}\sum_{\alpha,\beta=1}^m\int d\mathbf{r}\int d\mathbf{r}'\,\kappa_\alpha(\mathbf{r})P_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')\kappa_\beta(\mathbf{r})\right\}.\tag{3}$$

In writing Eq. (3), the replica density was introduced, defined as $\rho_\alpha(\mathbf{r})=\int_0^N dn\,\delta[\mathbf{r}_\alpha(n)-\mathbf{r}]$. The matrix $P_{\alpha\beta}(\mathbf{r},\mathbf{r}') = (1/\sigma_1^2)\delta(\mathbf{r}-\mathbf{r}')\delta_{\alpha\beta}\delta(z)\delta(z')-(\sigma_2^2/2)Q_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ contains a coupling term of two replicas, α and β, expressed through the overlap order parameter that measures the conformational overlap on the surface between two replicas,

segment interactions mediated by solvent
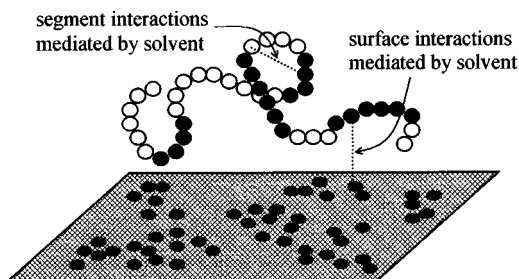
surface interactions mediated by solvent

FIG. 1. Schematic representation of the physical system considered. Interactions between the segments and between the segments and surface sites are indicated. The surface sites interact differently with the different polymer segments. All long-range interactions are mediated through the solvent.

$$Q_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \int_0^N dn\,\delta[\mathbf{r}_\alpha(n)-\mathbf{r}]\delta[\mathbf{r}_\beta(n)-\mathbf{r}']\delta(z)\delta(z').$$

The m-replica propagator, $\langle G^m\rangle_{\kappa,\theta}$, can be written as a functional integral over the density and overlap order parameter fields,

$$\langle G^m\rangle_{\kappa,\theta} = \int\int DQ_{\alpha\beta}\int\int D\rho_\alpha$$

$$\times\exp\{-E[Q_{\alpha\beta},\rho_\alpha]+S[Q_{\alpha\beta},\rho_\alpha]\},\tag{4}$$

where E and S are the effective energy and entropy of the system, respectively, given by

$$E[Q_{\alpha\beta},\rho_\alpha] = -\lim_{m\to 0}\frac{1}{m}\ln\prod_{\alpha=1}^m\int\int D\kappa_\alpha(\mathbf{r})$$

$$\times\exp\left\{-\frac{1}{2}\sum_{\alpha=1}^m\int d\mathbf{r}\int d\mathbf{r}'\,\kappa_\alpha(\mathbf{r})P_{\alpha\beta}(\mathbf{r},\mathbf{r}')\right.$$

$$\left.\times\kappa_\beta(\mathbf{r}')-\frac{v_0}{2}\int d\mathbf{r}\rho_\alpha^2(\mathbf{r})\right\}\tag{5}$$

and

$$S[Q_{\alpha\beta}, \rho_\alpha] = \lim_{m \to 0} \frac{1}{m} \ln \prod_{\alpha=1}^{m} \int \int D\mathbf{r}_\alpha(n)$$

$$\times \exp\left\{ -\frac{3}{2l} \sum_{\alpha=1}^{m} \int_0^N dn \left(\frac{\partial \mathbf{r}_\alpha}{\partial n} \right)^2 \right\}$$

$$\times \delta\left[\rho_\alpha(\mathbf{r}) - \int_0^N dn\, \delta[\mathbf{r}_\alpha(n) - \mathbf{r}] \right]$$

$$\times \delta\left[Q_{\alpha\beta}(\mathbf{r},\mathbf{r}') - \int_0^N dn\, \delta[\mathbf{r}_\alpha(n) - \mathbf{r}] \right.$$

$$\left. \times \delta[\mathbf{r}_\beta(n) - \mathbf{r}'] \delta(z)\delta(z') \right]. \tag{6}$$

A. Calculation of the effective energy

The calculation of the energy is analogous to the calculations outlined in Ref. 8, which amounts to calculating the Gaussian integral over $\kappa(\mathbf{r})$, with an additional term resulting from excluded volume segment-segment interactions. Here too, a one-step replica symmetry breaking (RSB) scheme is sufficient to predict a ''frozen'' phase where the configuration space of the RHP is determined by a few dominant conformations. Using this scheme, the effective energy per segment is calculated as

$$E = \frac{1}{2}\left[-\ln \sigma_1^2 + \frac{1}{x_0} \ln(1 - c_1 \bar{p} x_0) + v_0 \rho^2 \right], \tag{7}$$

where $\bar{p} = p/N$ is the fraction of the N polymer segments that are adsorbed to the surface. x_0 is an order parameter that equals unity when the polymer freely samples its configuration space. x_0 takes on values less than unity when the RHP samples a few energetically favorable conformations. $c_1 = \sigma_1^2 \sigma_2^2 N/A$ is proportional to the site loading on the surface with surface area A. Note that the excluded volume interactions give rise to ρ, the average density of segments far away from the surface, and are homopolymeric in nature. From Eq. (6), it is clear that this term is replica symmetric in nature and, therefore, can only qualitatively affect the frustrated nature of the system. Two order parameters are introduced from the RSB scheme, $\bar{p}$ and x_0. The former takes on finite values when the RHPs adsorb onto the surface; the latter takes on values less than unity when the RHPs are limited to sampling a subset of their configuration space.

B. Calculation of the effective entropy

The entropy in Eq. (6) can be calculated using physical arguments described below.[8,16,17] According to the Boltzmann equation, $S/k_B = \ln \Omega$, the entropy equals the logarithm of the number of distinguishable configurations of the system. In other words, Ω is the number of conformations in which x_0 replicas of an excluded volume chain can be arranged while having p contacts with surface sites such that they overlap perfectly on the surface *and* have the same density. Letting $f_{n_i}(\mathbf{R}_i - \mathbf{R}_{i-1})$ be the probability that a loop of length n_i begins at position $\mathbf{R}_{i-1}$ on the surface and ends at

$\mathbf{R}_i$ on the surface, the partition function of x_0 replicas of an adsorbed chain forming loops of various lengths ($n_i = 1...N$, with consecutive loops of $n_i = 1$ amounting to adsorbed ''trains'' on the surface) is given by

$$Z(N) = \sum_{n_i} \int d\mathbf{R}_1 \int d\mathbf{R}_2 \cdots \int d\mathbf{R}_p f_{n_1}^{x_0}(\mathbf{R}_1 - \mathbf{R}_0)$$

$$\times f_{n_2}^{x_0}(\mathbf{R}_2 - \mathbf{R}_1) \cdots f_{n_p}^{x_0}(\mathbf{R}_p - \mathbf{R}_{p-1})$$

$$\times \delta(n_1 + n_2 + \cdots + n_p - N). \tag{8}$$

The partition function for a train consisting of one unit is

$$f_1(\mathbf{s}_k) = \omega \delta(\mathbf{s}_k - \mathbf{l}\Delta_{jk}), \tag{9}$$

where $\mathbf{s}_k = \mathbf{R}_k - \mathbf{R}_{k-1}$. ω is the partition function for one adsorbed segment[25,26] taken to be a constant that depends on the properties of the chain; $\mathbf{l}$ is a two-dimensional vector whose length is that of a statistical segment; Δ_{jk} is a function that takes very small values if $\mathbf{s}_k$ crosses any pervious $\mathbf{s}_j$ vectors, otherwise it equals unity. Reference 27 provides a simple form for Δ_{jk} that is used in the following calculations.

The partition function of loops extending away from the surface can be derived from random walk statistics[28] and is the probability of forming a self-avoiding loop (assumed to be long) with its ends fixed to the surface, which is roughly,[29,30]

$$f_{n_i} \approx c R_0^{-3} \left(\frac{\mathbf{r}}{R_0} \right)^{5/2} \exp\left\{ -\left(\frac{\mathbf{r}}{R_0} \right)^{5/2} \right\}, \tag{10}$$

where R_0 is the end-to-end distance and scales as $n_i^{3/5} l$, and c is a normalization constant that is a measure of chain stiffness.

To solve for $Z(N)$, the Fourier transforms of Eqs. (9) and (10) are substituted into the Laplace transform of Eq. (8), approximating the sum over n_i's by an integral. After rigorous algebra, the following expression for the partition function is obtained:

$$Z(N) = \sum_{n=0}^{p} {}_n^p c^{nx_0} \omega^{(p-n)x_0} \frac{\Gamma^n\left(\dfrac{5 - 3x_0}{5} \right)}{\Gamma\left(\dfrac{5 - 3x_0}{5} n \right)}$$

$$\times [N - (p-n)]^{n(5-3x_0)/5 - 1}, \tag{11}$$

where $\Gamma()$ is the Gamma function, and ${}_n^p = \{p!/[n!(p-n)!]\}$.

The partition function above must be modified to account for the density constraint in Eq. (6), requiring that the probability that a polymer of length N subject to excluded volume interactions has an average density ρ, or, equivalently, stays within a sphere of a fixed diameter, D. Assuming that $D \gg l$, the excluded volume polymer can be modeled as a self-avoiding polymer of length N in a sphere with reflecting walls.[31] Since there are no energetics involved in this representation, the entropy loss due to confinement is simply $S_\rho/k_B = -\beta F$. The free energy, and thus the entropy, is a thermodynamically additive quantity and therefore is proportional to N, and scales as $N(l/D)^{5/3}$. As a rough estimate, the mean-field density is assumed to be determined by the effec-

tive energy expression alone. This is a good estimate in absence of the surface where self-avoiding walk statistics determine the size of the chain. This is a reasonable estimate for the average density of a weakly adsorbed polymer, where the surface interactions do not significantly alter the excluded volume polymer configuration. Thus, the average density is roughly determined by the number of segments per unit volume $[N/(4\pi R_g^3/3)]$. The sphere diameter can then be expressed in terms of the excluded volume parameter, v_0, and is approximately $6v_0^{3/4}/l^{5/4}$. The probability of confinement is $P_\rho = \exp[-S_\rho]$, and the entropy of x_0 replicas having the same density and the same overlap on the surface is (taking l to be of unit length) roughly

$$\frac{S}{N} = \frac{1}{N}\ln[P_\rho(N)Z(N)] \approx \frac{1}{x_0 N}\ln Z(N) + \frac{0.05}{v_0^{5/4}}. \qquad (12)$$

Combining Eq. (7) for the energy and Eqs. (11) and (12) for the entropy, the free energy per segment is calculated as

$$\frac{F}{N} = \frac{1}{2}\left[-\ln\sigma_1^2 + \frac{1}{x_0}\ln(1 - c_1\bar{p}x_0) + \rho^2 v_0\right]$$

$$-\frac{0.05}{v_0^{5/4}} - \frac{1}{x_0 N}\ln\sum_{n=0}^{p}{}_n^p c^{nx_0}\omega^{(p-n)x_0}$$

$$\times\frac{\Gamma^n\left(\dfrac{5-3x_0}{5}\right)}{\Gamma\left(\dfrac{5-3x_0}{5}n\right)}[N-(p-n)]^{n(5-3x_0)/5-1}. \qquad (13)$$

A mean field approximation is obtained by extremizing F with respect to the two order parameters, $\bar{p}$ and x_0.

III. RESULTS AND DISCUSSION

Figure 2 shows the variation of the adsorbed fraction ($\bar{p}$) and the freezing order parameter (x_0) as a function of surface site loading for heteropolymer solutions characterized by different excluded volume interactions. Each pair of curves is for a fixed value of v_0. In general, when there are only a few adsorbing sites on the surface ($c_1 \sim 0$), the adsorbed fraction is negligible and the freezing order parameter equals unity (the polymer is free to fluctuate between a large number of conformations) for all values of the excluded volume parameter. For a fixed value of v_0, each of the pairs of curves is characterized by a sharp adsorption transition accompanied by the freezing of the RHP into a few adsorbed conformations ($x_0 < 1$) at a threshold value of c_1. This recognition phenomenon has been established and observed in theory,[8] simulations,[9–11] and experiments.[2–6]

The interest of this paper lies in gaining qualitative information for practical applications. Therefore, the following discussion concentrates on the variation in $\bar{p}$ as an observable parameter. However, it is noteworthy to observe from Fig. 2 that x_0 consistently takes on values less than unity at the sharp adsorption transition for the RHPs characterized by different v_0. That is because the adsorption transition is a recognition transition between the polymer sequence distribution and the surface site distribution, and once the excluded volume interactions are overcome by the interactions
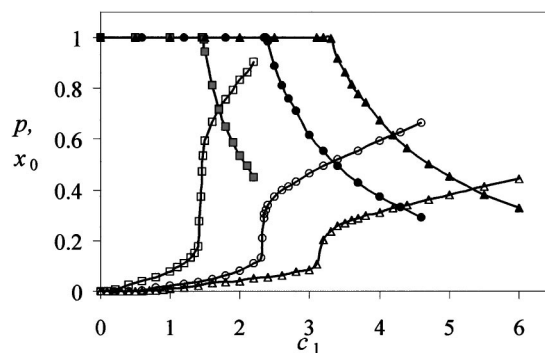

FIG. 2. Adsorbed fraction, $\bar{p}$ (open markers), and freezing parameter, x_0 (solid markers), as a function of surface site loading, c_1. Each $\bar{p}$ and x_0 pair is for the same value of the excluded volume parameter, v_0. $v_0 = 1$ for squares, $v_0 = 2$ for circles, and $v_0 = 3.5$ for triangles.

with the surface, the polymer strongly adsorbs. The configuration space of the adsorbed polymer is characterized by a few dominant low energy conformations separated by an energy gap form the higher energy conformations. On the other hand, the excluded volume interactions are non-specific homopolymeric in nature, and thus the free energy spectrum describing the polymer in the bulk is continuous.

With regards to the adsorption curves, the effect of increasing the excluded volume interactions is twofold. First, comparison of the adsorption curves in Fig. 2 reveals that solutions characterized by high values of v_0 show less distinguished adsorption transitions (i.e., the transition from the weakly adsorbed state to the strongly adsorbed state is less sharp), with a lower adsorbed polymer fraction after the transition. Second, the recognition transition occurs at increasing values of c_1 for increasing excluded volume interactions. The free energy, given by Eq. (13), contains two contributions from the excluded volume interactions. The energetic contribution increases while the entropic contribution decreases with increasing excluded volume interactions, and thus the overall free energy for a given polymer–surface system increases. Therefore, in order to overcome the increase in free energy for higher values of v_0, increasing attractive interactions with the surface (or higher site loadings) are needed for the polymer to strongly adsorb. The entropy decreases with increasing v_0 since the configuration space of the polymer is smaller. That is, the excluded volume interactions prohibit those conformations that allow for monomers to come in the immediate vicinity of other monomers, as is allowed in the freely fluctuating Gaussian chain. Thus, the entropic penalty of adsorption (arising from the limitation of the configuration space of the polymer to the adsorbed configurations) is lower for a polymer with lower bulk entropy.

Excluded volume interactions were shown to have a significant effect on the recognition transition of random heteropolymers. A ''good'' solvent, one that increases the excluded volume of the polymer, will tend to decrease the overall adsorbed polymer fraction. These results can be consequential for applications where recognition is important.[2–6] However, macromolecular adsorption may occur as a result of non-specific interactions with the surface, as is mostly the

case in protein deposition on membranes during filtration. The adsorption of proteins can lead to the formation of a thin film that is impermeable to both solvent and solute transfer through the membrane.[32–35] Furthermore, in some cases, the fouling species are valuable proteins or enzymes that may lose activity upon adsorption on the membrane's surface.[34] For such applications where polymer adsorption needs to be minimized, a solvent can be chosen such that the polymer at most only weakly adsorbs onto the surface. This corresponds, for example, to a solvent-polymer system characterized by $v_0 = 2$, as opposed to a system characterized by $v_0 = 1$ for a given surface characterized by $c_1 = 1$. Therefore, for these applications, system operation at solution conditions that reduce membrane fouling will improve efficiency and decrease operation costs, as well as increase the recovery of valuable solutes.

IV. CONCLUSION

We studied the pattern-recognition behavior of random heteropolymers as they interact with multifunctional surfaces. We have shown that solvent-mediated long-range interactions between polymer segments can influence the adsorption transition in two ways: stronger segment interactions lead to a lower final adsorbed polymer fraction, and a ''delay'' of the recognition transition to higher surface loading. Our theoretical results may help explain and predict phenomena observed in applications involving protein adsorption, such as protein fouling of membranes.

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