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Random copolymer adsorption onto a periodic heterogeneous surface: A partially directed walk model

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The adsorption of a single AB random copolymer (RC) chain onto an inhomogeneous ab surface with a regular periodic pattern is studied theoretically. The problem is considered within the simplest model of a partially directed random walk in two dimensions by using the method of generating functions and the annealed approximation for the averaging over disorder in the RC sequence. The existence of the "optimal" RC composition and the degree of correlation in the monomer sequence, at which the inverse transition temperature has a local minimum, is shown. This is characteristic for symmetric and weakly asymmetric surfaces, whereas for surfaces with pronounced asymmetry there is no such local minimum. The best adsorbate for a strongly asymmetric surface is the homopolymer composed of monomer units that are complimentary to the majority sites on the surface. The results for the adsorption transition point obtained in the annealed approximation are compared with the numerical results for random-periodic AB-copolymers with a long period being a quenched random sequence of A and B units. The comparison shows that the annealed approximation provides a very good quantitative estimate of the adsorption transition point.

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I. INTRODUCTION

The adsorption of polymer chains onto surfaces and interfaces [1–4] is a phenomenon that plays an important role in the stabilization of colloidal dispersions [5], surface modification [6], chromatography [7], the creation of polymer nanocomposites [8], etc. In many cases, the polymer and/or the surface can be chemically heterogeneous. The case in which both the polymer and the surface are heterogeneous is of particular interest because of the interplay between the distributions of monomer units in the heteropolymer and of sites on the surface [9,10]. This is closely related to the problem of molecular recognition, playing a central role in molecular biology as well as in polymer science aimed at creating biomimetic and "smart" polymer systems [11].

Recent developments of polymer synthesis have enabled us to obtain macromolecules with a predetermined sequence of comonomers, the so-called "sequence-defined polymers." This class of synthetic macromolecules resembles monodisperse polymers with a given sequence, such as proteins and nucleic acids. The synthesis of polymers with a predefined sequence opens up possibilities for the design of new heteropolymers that can selectively interact with the surfaces of globular proteins, cells, or viruses [12,13]. Using specially designed synthetic heteropolymers, it is possible to stabilize globular proteins, promote protein folding into a native biologically active structure, or inactivate viruses. For example, in [14], random heteropolymers formed by monomers of four types were designed to mimic intrinsically disordered proteins for protein solubilization and stabilization in a non-native environment. It was shown that heteropolymers with optimized composition and statistical distribution of monomers enable cell-free synthesis of membrane proteins with correct protein folding in solution. In [15], a coarse-grained computer simulation of two-letter random copolymers interacting with several globular proteins was carried out. Random copolymers were shown to efficiently encapsulate proteins to optimize their enzymatic activity. It has been found that the adsorbed polymer chains have very similar sequences, indicating that proteins are able to "select" certain sequences that best reduce their solvent exposure. In [16], the effect of the primary sequence on complex formation between oppositely charged polypeptides was analyzed, and it was demonstrated that the sequence specificity of charged monomers can be used to accurately control the self-assembly and thermodynamics of complex coacervates. Hence, unraveling the regularities of heteropolymers' binding to heterogeneous surfaces has both fundamental and practical importance.

The adsorption of heteropolymers onto heterogeneous surfaces has been studied theoretically in numerous works by using methods of analytical theory and computer simulation. In particular, in the series of works by Chakraborty *et al.* [9,17–21], the adsorption of a single macromolecule of a statistical heteropolymer on a statistically inhomogeneous surface was studied analytically and by Monte Carlo simulation. It was found that adsorption occurs in two stages that include heteropolymer binding to the surface and its "freezing" on the surface in order to maximize the number of energetically favorable contacts. It was also found that heteropolymers can "recognize" multifunctional disordered surfaces if the statistics characterizing the distribution of monomer units in the heteropolymer and the distribution of

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sites on the surface are related in a certain way, exhibiting so-called statistical pattern matching. In [10,22], Monte Carlo simulation of a random copolymer adsorption on a random surface containing sites of two types, where both the monomer sequence and the surface sites distribution contain correlations, was performed. It was shown that statistically random, uncorrelated surfaces are insensitive to correlations in the monomer sequence of the random copolymer. Similarly, statistically random heteropolymers do not distinguish between different surface types. However, when neighboring surface sites are statistically correlated, selective adsorption of random heteropolymers is observed—random copolymers with a similar type of correlation are preferentially adsorbed onto the surface. These conclusions agree with the theoretical results obtained for the continuum Gaussian heteropolymer model [23] and the partially directed two-dimensional polymer model [24].

At the same time, the adsorption of random heteropolymers onto chemically inhomogeneous surfaces with a *regular periodic pattern* has not been studied yet to the best of our knowledge. The aim of the present work is to start filling this gap. The problem will be solved in the framework of the two-dimensional partially directed walk (2D-PDW) model of the polymer. This model is the *minimal model* for studying the interaction of a heteropolymer with a heterogeneous surface, in which the polymer may "adjust" to the heterogeneous surface pattern. The 2D-PDW model has been successfully used to investigate the adsorption of a random copolymer (RC) on a random surface in the annealed approximation [24,25] and a periodic copolymer on a periodic inhomogeneous surface [26] by using the generating functions (GF) approach.

The random sequence of monomer units in the RC is *quenched*, which means that after the synthesis of the RC macromolecule, its monomer sequence remains unchanged. To find the quenched free energy F_q, it is necessary to average the partition function Z over all realizations of a random sequence: $F_q = -k_B T \langle \ln Z \rangle$, where angular brackets $\langle \ldots \rangle$ denote averaging over the ensemble of random sequences, or disorder average, k_B is the Boltzmann constant, and T is the temperature. Averaging $\ln Z$ is a rather difficult problem (if solvable at all), therefore one has to resort to approximation schemes, such as the celebrated replica trick [27,28].

Direct averaging of the partition function prior to taking its logarithm corresponds to the *annealed* type of disorder and a fundamentally different physical situation, when averaging over random sequence realizations is carried out simultaneously with averaging over conformations. As a result, the type of any monomer unit in the RC sequence and, accordingly, its affinity to the surface can change when the system reaches equilibrium [29]. The annealed approximation does not guarantee that even the lower moments of the monomer distribution remain correct in the final result. The annealed free energy $F_a = -k_B T \ln \langle Z \rangle$ gives a lower bound on the quenched free energy (by the arithmetic mean–geometric mean inequality) and it can roughly be considered as the "zero-order" approximation to the quenched average.

Nevertheless, the solution of the problem within the framework of the annealed approximation can be useful; in particular, the annealed estimate of the adsorption-desorption transition point is quite reasonable in many cases. Moreover, as is known in the case of RC adsorption onto a homogeneous surface, refinement of the annealed approximation by imposing constraints on the moments of the monomers distribution in the RC sequence known as the Morita approximation [30,31] gives the same position of the transition point [32,33]. For some pinning and wetting models, this was rigorously proven by Caravenna and Giacomin [34]. One can expect that the same should hold for the case considered in the present study.

At the same time, there is no *a priori* reason to expect that the annealed and quenched critical points will be identical or even close, and one should use the annealed estimate of the transition point with caution. As a counterexample, we can mention here the problem of RC localization at an interface between two immiscible liquids [35], where the use of the annealed approximation leads to a qualitatively incorrect phase diagram, which, however, can be substantially improved by introducing the Morita conditions [36].

In the present work, we will focus on the adsorption transition point and its dependence on the distribution of monomer units and sites in the RC and on the heterogeneous surface, respectively. To check the correctness of the adsorption transition point obtained in the annealed approximation, we also calculate the transition point for a quenched system with particular realizations of the random sequence. Specifically, we consider a *random periodic copolymer*, i.e., a regular periodic copolymer with a long period, which is a random monomer sequence. The GF method gives an exact solution for a regular periodic copolymer on a periodic inhomogeneous surface in the framework of the 2D-PDW model [26].

The rest of the paper is organized as follows. Section II defines the model and introduces the annealed approximation and the GF approach. The results are presented in Sec. III. In particular, we discuss the adsorption transition point in the symmetric case (Sec. III B), and the effects of the RC and the periodic surface asymmetry (Secs. III E and III F), and we check the validity of the annealed approximation for the adsorption transition point by comparing the results with numerical solution for a random periodic copolymers (Sec. III G). Finally, Sec. IV presents the summary and our concluding remarks.

II. MODEL AND METHOD

A. Definition of the model

Consider a RC chain composed of A and B monomer units interacting with a heterogeneous surface that carries a and b sites, Fig. 1. RC conformations are modeled as 2D-PDWs on the square lattice, therefore the adsorbing surface is simply a line. The monomer sequence of the RC is given by $\chi = \{\chi_1, \chi_2, \ldots, \chi_n\}$, where $\chi_i = A$ or B while the surface pattern is given by $\sigma = \{\ldots, \sigma_1, \sigma_2, \sigma_3, \ldots\}$, where $\sigma_i = a$ or b. Monomer units in the RC are distributed randomly and are modeled as a first-order Markov chain. It is defined by the probabilities to find A and B monomer units in the sequence $P(\chi_m = A) = f_A$, $P(\chi_m = B) = f_B = 1 - f_A$, and by the probabilities that a monomer of type i is followed by a monomer of type j, $P(\chi_m = j|\chi_{m-1} = i) = p_{ij}$. The transition probabilities are normalized: $\sum_j p_{ij} =$

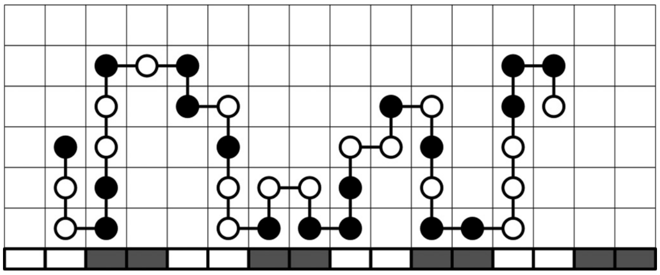

FIG. 1. 2D partially directed walk model of a random copolymer consisting of A (white) and B (black) monomer units near a linear (planar) periodic surface composed of a (white) and b (gray) sites.

1. It is also assumed that the Markov chain is reversible, i.e., $f_i p_{ij} = f_j p_{ji}$. The correlation parameter $c_p = 1 - p_{AB} - p_{BA} = p_{AA} + p_{BB} - 1$ determines the character of correlations in the monomer sequence: $c_p > 0$ indicates that there is a tendency in the sequence for grouping similar monomers into clusters, $c_p < 0$ favors the alternating sequence of A's and B's, and $c_p = 0$ corresponds to uncorrelated (Bernoullian) sequences. The probability of a particular realization of the sequence χ is given by the product $P(\chi) = f_{\chi_1} \times p_{\chi_1\chi_2} \times p_{\chi_2\chi_3} \times \cdots \times p_{\chi_{n-1}\chi_n}$.

Because of the normalization and reversibility conditions, the Markov chain is completely defined by just two independent parameters. If f_A and c_p are chosen as these parameters, then the transition probabilities are $p_{AA} = f_A + c_p(1 - f_A)$, $p_{AB} = (1 - f_A)(1 - c_p)$, $p_{BA} = f_A(1 - c_p)$, and $p_{BB} = 1 - f_A + c_p f_A$. The range of possible values for f_A depends on the correlation parameter c_p: for $c_p \geqslant 0$ it can accept any value within the range from 0 to 1, whereas for $c_p < 0$ this range depends on c_p: $-c_p/(1 - c_p) < f_A < 1/(1 - c_p)$.

In contrast to the RC, a and b sites on the heterogeneous surface are distributed nonrandomly and form a regular periodic sequence that has the structure $(a_{\ell_a}, b_{\ell_b})_x$ of alternating blocks of a- and b-sites with the lengths ℓ_a and ℓ_b, respectively. $m_s = \ell_a + \ell_b$ is the surface period size.

The partition function of this system can be written as follows [25]:

$$Z_n(\beta|\chi,\sigma) = \sum_{\mathbf{r}_i} \exp\left[-\beta \sum_{i=1}^{n} \delta_{y_i,0}\, \epsilon_{\chi_i \sigma_{x_i}}\right], \tag{1}$$

where $\mathbf{r}_i = \{x_i,\ y_i\}$, $i = 1, \ldots, n$ denotes the chain conformation (positions of the monomer units on the 2D square lattice), δ_{ij} is the Kronecker delta, ϵ_{ij} is the energy of the monomer-surface contact ($i \in \{A,\ B\}$ and $j \in \{a,\ b\}$), and $\beta = 1/k_B T$ is the inverse temperature.

B. Annealed approximation and generating functions approach

We solve the problem in the annealed approximation, where the quenched free energy $\beta F_q = -k_B T \langle \ln Z_n(\beta|\chi,\sigma)\rangle_\chi$ obtained by averaging the logarithm of the partition function over all possible realizations of the RC is approximated by the annealed free energy $\beta F_a = -k_B T \ln\langle Z_n(\beta|\chi,\sigma\rangle_\chi$, where the partition function is averaged prior to taking the logarithm.

To calculate the annealed partition function, $\langle Z_n(\beta|\chi,\sigma)\rangle_\chi$, we use the GF approach. In the case of the RC adsorption onto a heterogeneous surface, this approach consists in calculating the GF,

$$G(z,t) = \sum_{n=1}^{\infty}\sum_{m=1}^{n} \langle Z_{n,m}(\beta|\chi,\sigma)\rangle_\chi\, z^n t^m, \tag{2}$$

where $Z_{n,m}(\beta|\chi,\sigma)$ is the constrained partition function of a chain with n monomer units and the length of the chain projection onto adsorbing surface equal to m. The GF variables z and t are conjugated to the chain length and the chain projection, respectively. The smallest singularity of $G(z,t)$ calculated at $t = 1$ gives the asymptotic expression for the partition function in the large n limit: $\langle Z_n(\beta|\chi,\sigma)\rangle_\chi \simeq z_c^{-n}(t = 1)$.

For the 2D-PDW model of a RC adsorption onto a random heterogeneous surface, it was shown [24] that the smallest GF singularity is determined by the solution of the following determinant equation:

$$\det[\mathbf{E} - \mathbf{G}_L(z,\ t)\mathbf{G}_S(z,\ t)]_{t=1} = 0. \tag{3}$$

Here $\mathbf{G}_S(zt)$ and $\mathbf{G}_L(z,\ t)$ are the GFs of adsorbed sequences (or trains) and loops, respectively, in matrix form:

$$\mathbf{G}_S(zt) = \sum_{n=1}^{\infty} \Omega_S(n)(zt)^n \mathbf{R}^n, \tag{4}$$

$$\mathbf{G}_L(z,\ t) = \sum_{n=2}^{\infty}\sum_{m=2}^{n} \Omega_L(n,\ m) z^n t^{m-2} (\mathbf{P}^n \otimes \mathbf{S}^{m-2}), \tag{5}$$

where $\Omega_S(n)$ is the number of trains of length n, and $\Omega_L(n,\ m)$ is the number of loops of the contour length n and the length m of the loop projection to the surface (the factor $m - 2$ instead of m stands here because of the overlap between projections of loops and tails [24]). t is the auxiliary variable conjugate to the length of the chain projection onto the surface.

The matrices $\mathbf{P}$ and $\mathbf{S}$ are the transition probability matrices for the heteropolymer and the heterogeneous surface, respectively. For the RC, the matrix $\mathbf{P}$ is

$$\mathbf{P} = \begin{pmatrix} p_{AA} & p_{AB} \\ p_{BA} & p_{BB} \end{pmatrix} = \begin{pmatrix} p_{AA} & 1 - p_{AA} \\ 1 - p_{BB} & p_{BB} \end{pmatrix}. \tag{6}$$

The periodic heterogeneous surface can be considered as a special case of a random surface with m_s different surface site types $S_1, S_2, S_2, \ldots, S_{m_s}$. In terms of the first-order Markov chain, the transition probability matrix $\mathbf{S}$ for this strictly periodic *quenched* sequence takes the form

$$\mathbf{S} = \begin{pmatrix} 0 & 1 & 0 & \cdot & 0 \\ 0 & 0 & 1 & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \cdot & 1 \\ 1 & 0 & 0 & \cdot & 0 \end{pmatrix} \tag{7}$$

with unit entries in the upper subdiagonal. The matrix $\mathbf{S}$ has the dimensions $m_s \times m_s$. This is a *circulant matrix.*

The matrix $\mathbf{R}$ is defined as

$$\mathbf{R} = (\mathbf{P} \otimes \mathbf{S}) \cdot \mathbf{W} \tag{8}$$

with the $(2m_s) \times (2m_s)$ diagonal "interaction matrix"

$$\mathbf{W} = \mathrm{diag}(w_{11}, w_{12}, \ldots, w_{1m_s}, w_{21}, w_{22}, \ldots, w_{2m_s}) \tag{9}$$

containing all statistical weights of different monomer-surface contacts, $w_{ij} \equiv e^{-\beta\epsilon_{ij}}$, where $i \in \{1,\ 2\}$ and (that is,

$i \in \{A, B\}$) $j \in \{1, 2, \dots, m_s\}$ (that is, $j \in \{S_1, S_2, \dots S_{m_s}\}$). The particular periodic structure of the heterogeneous surface is set by properly defining the elements of the diagonal interaction matrix **W** [24,26].

Matrix GFs of trains and loops, Eqs. (4) and (5), can be calculated by using eigenvalues and eigenvectors of the matrices **P**, **S**, and **R** and by exploiting the expressions for the corresponding scalar GFs:

$$G_S(z) = z^2 + z^3 + \cdots = \frac{z^2}{1-z}, \tag{10}$$

$$G_L(z,t) = \frac{1 - zt - z^2 - z^3t - \sqrt{(1 - zt - z^2 - z^3t)^2 - 4z^4t^2}}{2z^2t^2}; \tag{11}$$

see [24] for details. Moreover, the matrix GF for trains $\mathbf{G}_S(zt)$ can be calculated directly as [26]

$$\mathbf{G}_S(zt) = z^2t^2\mathbf{R}^2[\mathbf{E} - zt\mathbf{R}]^{-1}, \tag{12}$$

where $[\dots]^{-1}$ stands for the matrix inverse.

At the transition point, $\beta = \beta_{tr}$ the smallest singularity z_c associated with the adsorbed state of the chain should be equal to the smallest singularity of the GF for the free (desorbed) chain, $z_V = \sqrt{2} - 1$ [37], hence the transition point is determined from the equation

$$\det[\mathbf{E} - \mathbf{G}_L(z_V, 1)\mathbf{G}_S(z_V)] = 0. \tag{13}$$

The transition point is obtained by solving Eq. (13) with respect to β numerically.

III. RESULTS AND DISCUSSION

A. Choosing the system parameters

The system under study depends on a large number of parameters: four of them define the primary structure of the RC monomer sequence (f_A and c_p) and of the periodic surface (ℓ_a and ℓ_b), the other five are the polymer-surface interaction energies (ϵ_{Aa}, ϵ_{Ab}, ϵ_{Ba}, ϵ_{Bb}) and the temperature T [or inverse temperature $\beta = 1/(k_BT)$] that define the statistical weights of all possible monomer-surface contacts. Therefore, we adhere to the choice made in previous works [24–26] by taking the inverse temperature β as a separate control variable and keeping monomer-surface energies fixed. Specifically, we consider *Aa* and *Bb* contacts as favorable, $\epsilon_{Aa} = \epsilon_{Bb} = -1$, and *Ab* and *Ba* contacts as neutral $\epsilon_{Aa} = \epsilon_{Bb} = 0$. We will use this set of interaction energies throughout the article. In Sec. IV we briefly discuss other sets of the interaction energies.

B. Adsorption transition point in the symmetric case

Traditionally, random and regular copolymer adsorption on inhomogeneous surfaces is studied primarily for copolymers and surfaces of *symmetric* composition (that is, with equal fractions or equal probability of appearance, of monomer units and surface sites of different types) [10,17–19,22,24,26,38]. Following this tradition, we also begin our discussion with the symmetric case, when $f_A = 0.5$ in the RC and $\ell_a = \ell_b = \ell$ on the periodic surface.

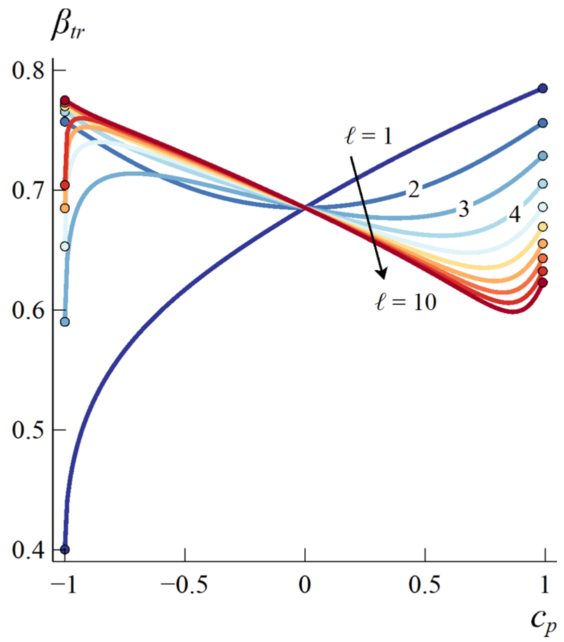

FIG. 2. Inverse transition temperature in the annealed approximation as a function of RC correlation parameter for symmetric RC ($f_A = 0.5$) adsorbing onto the periodic symmetric surface with $\ell_a = \ell_b = \ell = 1, \dots, 10$ as indicated.

For the smallest possible $\ell = 1$, the dependence of the inverse transition temperature $\beta_{\rm tr}$ on the RC correlation parameter c_p, Fig. 2, is a monotonically increasing function of c_p indicating that the lowest inverse transition temperature is reached at $c_p = -1$, which corresponds to the regular alternating *AB*-copolymer that fits perfectly the symmetric periodic surface with $\ell = 1$. At the same time, this reflects the general trend for the symmetric RC adsorption on a symmetric random surface [24]: if the surface correlation parameter is negative, then the lowest inverse transition temperature corresponds to $c_p = -1$. On the contrary, when the correlation parameter has a positive value, the smallest inverse transition temperature is reached at $c_p = 1$. That is, in both cases, the smallest inverse transition temperature corresponds to the limiting values of c_p, and the $\beta_{\rm tr}(c_p)$ dependence has a boundary minimum.

For the RC adsorption on symmetric regular surfaces with $\ell > 1$, the situation changes dramatically. A local minimum appears on the $\beta_{\rm tr}(c_p)$ dependence, which means that there exists an "optimal" correlation parameter in the RC with the lowest inverse transition temperature. For $\ell = 2$ the position of the minimum is at $c_p = 0$. As the surface period ℓ increases, the position of the local minimum shifts to larger c_p. This is easily understood: the structure of the monomer sequence in the RC must match the periodic surface pattern, and the larger the surface period ℓ is, the more blocky the RC should be to "recognize" it.

Note that in the case of the RC adsorption onto a *random* surface (in the case of the 2D-PDW model, when both the polymer and the surface are the first-order Markov chains), no local minimum is observed [24]. It is also interesting to note that RCs with Bernoullian (uncorrelated) monomer sequences show insensitivity to the correlations on the surface (that is,

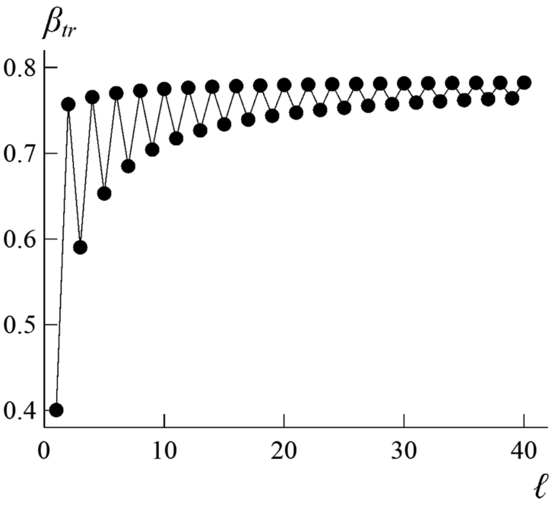

FIG. 3. Inverse transition temperature for alternating copolymer (RC with $f_A = 0.5$ and $c_p = -1$) adsorbing onto the periodic symmetric surface with $\ell_a = \ell_b = \ell$ as a function of ℓ.

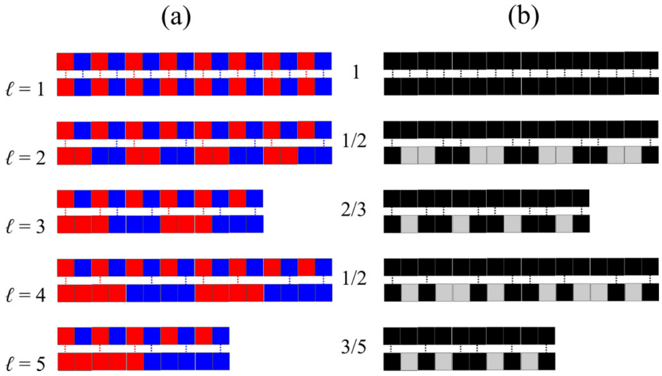

FIG. 4. Schematic pictures of the alternating copolymer extended over a periodic surface with $\ell_a = \ell_b = \ell = 1, \ldots, 5$ (a) and mapping of these systems to a homopolymer adsorbing onto a periodic surface with the attractive (black) and the nonattractive site (b). Attractive, or good, contacts are shown by vertical dotted lines. For each ℓ, the upper bound for the fraction of good contacts, q, is indicated between panels (a) and (b).

period size ℓ)—we see that all curves in Fig. 2 have a common point at $c_p = 0$.

For symmetric surfaces with odd $\ell = 1, 3, 5, 7, 9$ there is also a boundary minimum at $c_p = -1$. At $\ell = 1$ and 3 this minimum dominates, whereas at odd $\ell \geqslant 5$ it becomes a minor minimum and the local minimum dominates. In the case of surfaces with even ℓ, there is no additional boundary minimum but only a local minimum.

C. On the alternating *AB*-copolymer adsorption onto a periodic symmetric surface

To understand the appearance of the boundary minimum at odd ℓ in Fig. 2, consider the dependences of the transition point for $c_p = -1$ and different ℓ for the periodic surface; these are shown in Fig. 3. Recall that the RC with $c_p = -1$ corresponds to the special case of a strictly alternating *AB*-copolymer, i.e., the periodic copolymer (...*ABABABAB*...). It can be seen that the dependence of the transition point on ℓ is nonmonotonic. There are regular oscillations with the period 2 and decaying amplitude, minima at odd ℓ, and maxima at even ℓ. One can extract two subdependences $\beta_{\rm tr}(\ell)$ for even and odd ℓ, respectively. As the period length increases, these two subdependences approach each other and the amplitude of the oscillations decreases. This explains the appearance of an edge minimum at odd ℓ and its dominance at small odd ℓ.

The nature of such oscillations can be understood by taking into account the following peculiarity of the 2D-PDW model: if we number the monomer units in the chain and the sites on the surface (from 1 to n) and bring the monomer 1 and the site 1 in contact, then the indices of contacting monomer units and surface sites will have necessarily the same parity. In the alternating copolymer, all sites with odd indices are of the same type (for example, A) and all sites of even indices are of a different type (correspondingly, B). Therefore, each odd-numbered surface site may have a contact with A-monomer only, and each even-numbered surface site may have a contact with B-monomer only. As a result, each surface period can provide a certain number of good contacts, the fraction of which cannot exceed some limit. This upper bound for the fraction of good contacts, which we denote by q, can easily be determined by considering the interactions of an alternating copolymer chain extended above the symmetric periodic surface with the period $m_s = 2\ell$. This is illustrated by Fig. 4, where such interactions are shown for five cases with $\ell = 1, \ldots, 5$, respectively. All good contacts between the alternating polymer and the symmetric periodic surface are marked by vertical dashed lines. Each such pair (alternating copolymer + symmetric periodic surface) can be mapped to the homopolymer adsorbing on an inhomogeneous periodic surface; such mapping is shown in Fig. 4(b). We see that the fraction of attractive sites on this periodic surface [which is equal to the maximum fraction of good contacts per surface period (2ℓ) in the original system, or the upper bound q] behaves nonmonotonically: for even ℓ it is equal to 1/2, while for odd $\ell = 2n - 1$ ($n > 0$) it depends on ℓ as $q = n/(2n - 1) = (\ell + 1)/(2\ell) = 1/2 + 1/(2\ell)$, thus decreasing from 1 at $\ell = 1$ and tending asymptotically to 0.5 from above. This explains the decay of the oscillation amplitude on the ℓ-dependences of the transition point, Fig. 3, and the corresponding growth of $\beta_{\rm tr}$ with increasing period length at odd ℓ. In the case of even ℓ, q is always equal to 0.5 but the surface pattern becomes more "dilute," and this also leads to the weak growth of $\beta_{\rm tr}$ with increasing ℓ.

D. Effect of the RC asymmetry on the adsorption transition point

Consider now how the asymmetry of the RC composition affects the position of the adsorption transition point if the inhomogeneous surface still remains symmetric ($\ell_a = \ell_b = \ell$). The RC composition is determined by the probability f_A of the A unit occurrence in the RC monomer sequence. We have taken into account all possible RC compositions $0 < f_A < 1$ and the whole accessible range of the correlation parameter, c_p, for each f_A. The upper limit of this range is 1, whereas the

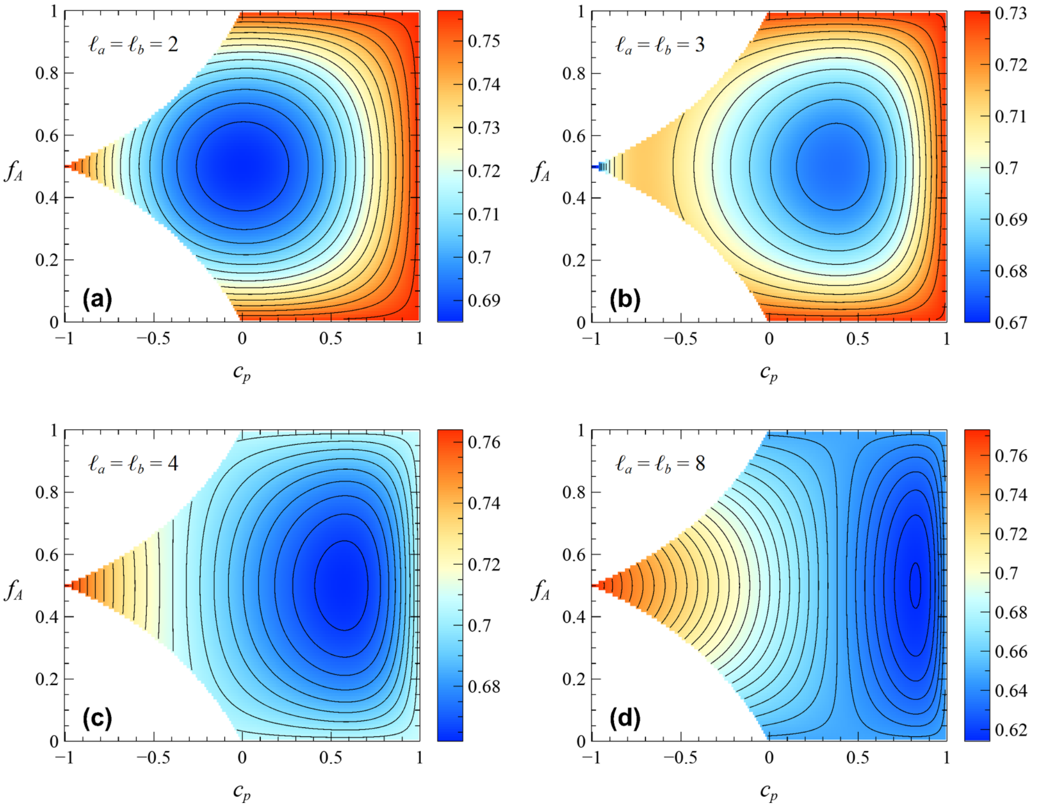

FIG. 5. Inverse transition temperature as a function of the RC correlation parameter c_p and the A-monomer unit probability f_A presented as density plot for a RC adsorbing onto the periodic symmetric surface with $\ell_a = \ell_b = 2$ (a), 3 (b), 4 (c), and 8 (d).

lower limit depends on f_A:

$$\max\left(-\frac{f_A}{1-f_A}, -\frac{1-f_A}{f_A}\right) < c_p < 1. \tag{14}$$

For each pair (c_p, f_A), the inverse transition temperature β_{tr} was calculated. The results are presented in Fig. 5 in the form of a density map in the coordinates (c_p, f_A). The boundaries of the "forbidden" range of parameter values according to Eq. (14) are clearly seen on these contour maps. These are

$$f_A = -\frac{c_p}{1-c_p} \text{ and } f_A = \frac{1}{1-c_p}, \ -1 \leqslant c_p \leqslant 0. \tag{15}$$

Thus, we consider the whole ensemble of random sequences interacting with the given periodic inhomogeneous surface trying to find a combination of f_A and c_p corresponding to the lowest inverse temperature in the adsorption transition point. Such a pair (c_p, f_A) can be called "optimal," which "recognizes" a given inhomogeneous surface better than others. Due to the symmetry of the surface, the density maps in Fig. 5 are symmetric with respect to the axis $c_p = 0$.

Figures 5(a)–5(d) show that the lowest value of the inverse transition temperature is observed at $f_A = 0.5$, that is, a symmetric surface is better recognized by a RC with the symmetric composition. Increasing the asymmetry of the RC composition shifts the transition point toward larger β thus deteriorating the RC binding to the surface. This is clear because only in the case $f_A = 0.5$ is it possible to form the largest number of thermodynamically favorable Aa and Bb contacts (if we broke the links between monomer units, they could all form good contacts with the surface sites, and the fraction of good contacts would be equal to 1). In the case $f_A < 0.5$, it is possible to form $0.5 + f_A$ good contacts: all b-sites can be occupied by B monomer units, and the fraction of Bb contacts can reach 0.5, whereas the fraction of Aa contacts cannot exceed f_A. Thus, $0.5 - f_A$ of a surface sites and the same fraction B-units would remain unoccupied/unbound. If $f_A > 0.5$, the largest possible fraction of good contacts is $0.5 + (1 - f_A)$.

With an increase in the surface period, the position of the local minimum (at $f_A = 0.5$) shifts to larger c_p. At $\ell = 3$, there is also a boundary minimum observed at $c_p = -1$, which is the dominant one; see also Fig. 2. A similar boundary minimum is observed for odd $\ell > 3$. These findings are consistent with the data presented in Fig. 2.

Hence, we can conclude that a compositionally symmetric RC demonstrates the best ability to adsorb on a periodic symmetric surface; the optimal degree of correlation c_p corresponding to the lowest β_{tr} is determined by the period length ℓ on the surface.

E. Effect of the periodic surface asymmetry on the adsorption transition point

The effect of the periodic surface asymmetry on the RC adsorption transition point is illustrated by Figs. 5(c) and 6. Here the a-block length, ℓ_a, is kept fixed at $\ell_a = 4$, whereas

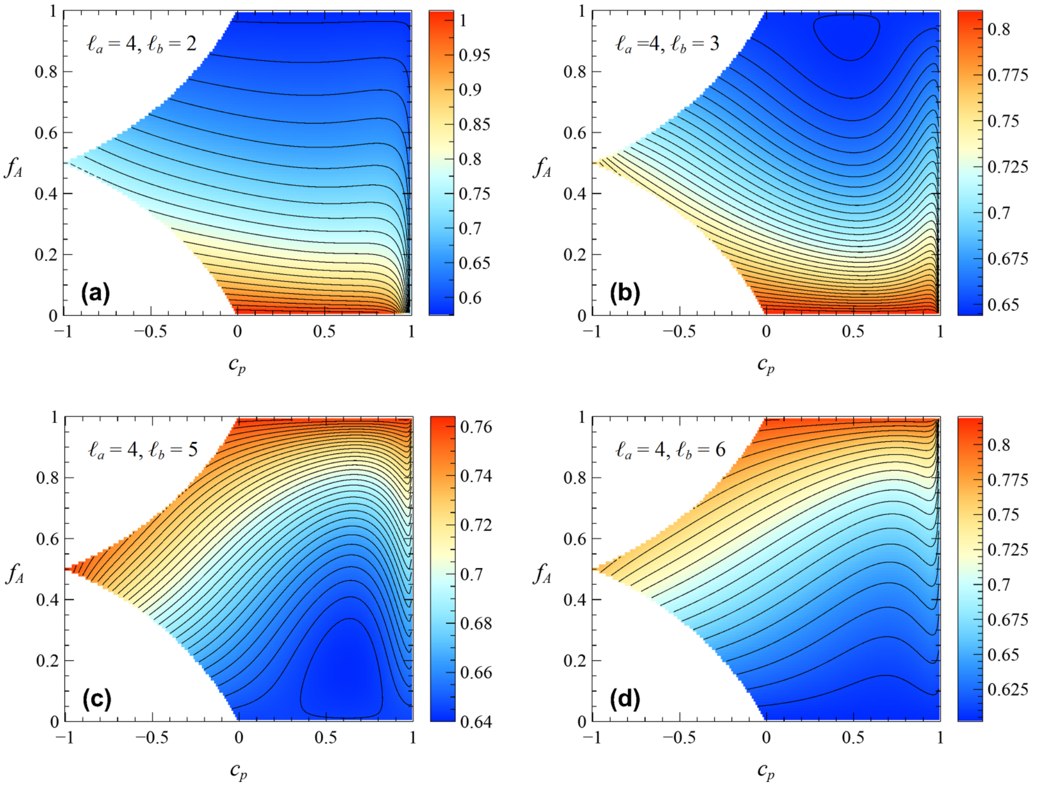

FIG. 6. Inverse transition temperature as a function of the RC correlation parameter c_p and the A-monomer unit probability f_A presented as a density plot for a RC adsorbing onto the periodic asymmetric surface with $\ell_a = 4$ and $\ell_b = 2$ (a), 3 (b), 5 (c), and 6 (d).

the b-block width, ℓ_b, is varied. We can see that only in the case of a symmetric ($\ell_b = \ell_a = 4$) and a weakly asymmetric ($\ell_b = 3$ or 5) surface is there a nontrivial local minimum with $0 < f_A < 1$. On the density plot, for $\ell_b > \ell_a$ ($\ell_b < \ell_a$) the local minimum shifts towards smaller (larger) f_A, so the system maximizes the number of possibilities to form energetically favorable Aa and Bb contacts. For surfaces with pronounced asymmetry ($\ell_b \leqslant 2$ or $\ell_b \geqslant 6$ at $\ell_a = 4$), the local minimum becomes the boundary one corresponding to the homopolymer A [if $\ell_a > \ell_b$, Fig. 6(a)] or B [if $\ell_a < \ell_b$, Fig. 6(d)]; the particular value of the correlation parameter c_p in this case has a purely formal character since it does not have any effect on the homopolymer composition.

The dependence of the local minimum position in the coordinates (c_p, f_A) on the variation in ℓ_a and ℓ_b is illustrated by Fig. 7. We see that increasing ℓ_a leads to the increase in the range of ℓ_b at which a local minimum exists. With increasing ℓ_b (provided that ℓ_a is fixed), the position of the minimum moves to smaller f_A and to larger c_p (we have already discussed that for $\ell_a = 4$). The points corresponding to the same difference $\Delta\ell = \ell_a - \ell_b$ are grouped into individual dependences. For $\ell_a = \ell_b$ all the points lie on the line $f_A = 0.5$, for $\Delta\ell < 0$ ($\ell_a < \ell_b$) f_A increases with c_p, and for $\Delta\ell > 0$ ($\ell_a > \ell_b$) f_A decreases with c_p.

It is also interesting to look at the local minimum value of the inverse temperature in the transition point; these are shown in Fig. 8. We see that there is a general trend of decreasing $\beta_{\rm tr}^{(\rm min)}$ with increasing period. Starting from $\ell_a = 3$, when there are at least three values of ℓ_b giving a local minimum, the dependence of $\beta_{\rm tr}^{(\rm min)}$ on ℓ_b is nonmonotonic and has a maximum at $\ell_b = \ell_a$. That is, the "recognition" of an asymmetric

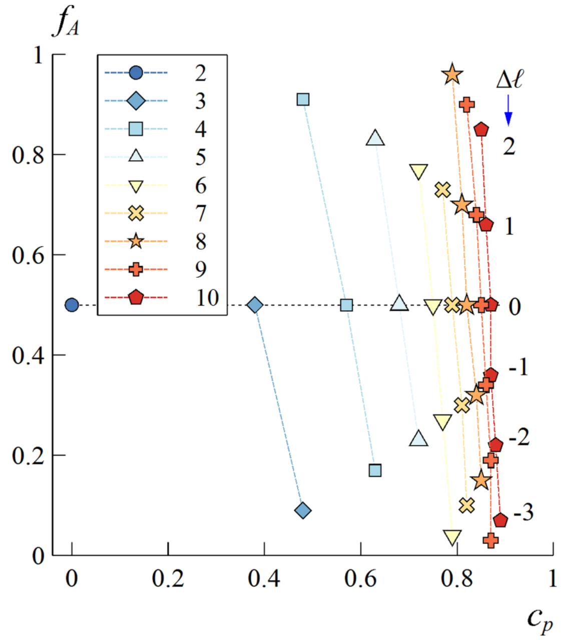

FIG. 7. Position of the minimum of the inverse transition temperature on the (c_p, f_A) plane for a RC adsorbing onto the periodic asymmetric surface with $\ell_a = 2, 3, \ldots, 10$ and $\Delta\ell = \ell_a - \ell_b$ as indicated.

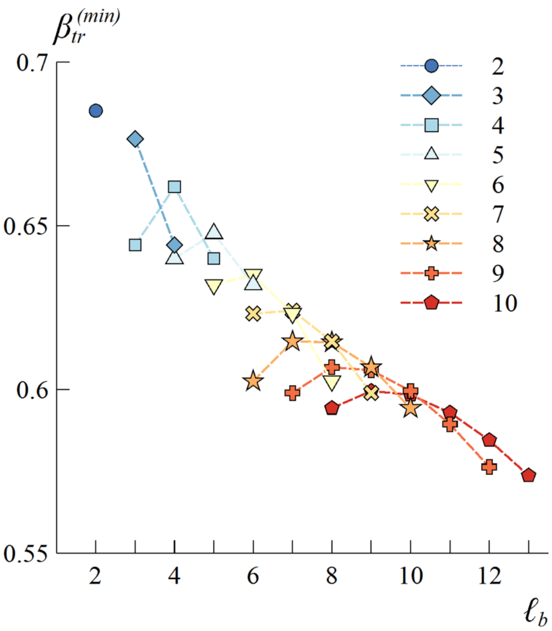

FIG. 8. The value of the inverse transition temperature in the local minimum as a function of the nonadsorbing b-block width ℓ_b for a RC adsorbing onto the periodic asymmetric surface with $\ell_a = 2, 3, \ldots, 10$ as indicated.

surface by asymmetric random copolymers occurs at a lower inverse temperature than in the symmetric case.

F. On the validity of the annealed approximation for the adsorption transition point

The adsorption transition point discussed above was obtained in the annealed approximation. One of the options to check its validity is to solve the problem numerically for a chain of finite length by taking a set of the RC monomer sequence realizations. For the 2D-PDW model, one can use the transfer matrix approach, as was done for the SRW chain model in [32]. We suggest, however, another idea, which, as far as we know, has not been implemented yet: The GF method gives an exact solution for a periodic copolymer adsorbed on an inhomogeneous periodic surface, in the infinite chain limit, regardless of the specific structure of the periods in the monomer sequence and on the surface [26]. Therefore, one can take a periodic copolymer with a rather long period, where the period itself is a *random sequence* of monomer units corresponding to a certain probability distribution (the first-order Markov chain in our case). Because of the large period length, much larger than the monomer sequence correlation length ξ (for the first-order Markov chain it is related to the correlation parameter c_p as $\xi = -1/\ln c_p$ [39]; for example, $\xi \approx 9.5$ for $c_p = 0.9$ and $\xi \approx 4.5$ for $c_p = 0.8$), the chain “loses” information about monomer-monomer correlations on such a large scale.

The periodic copolymer with the random structure of its period can be called a “random-periodic copolymer” (RPC). Here we use the same approach as for the RC in the annealed approximation, with the 2×2 transition probability matrix $\mathbf{P}$ replaced by the $m_p \times m_p$ circulant matrix of the form (7).

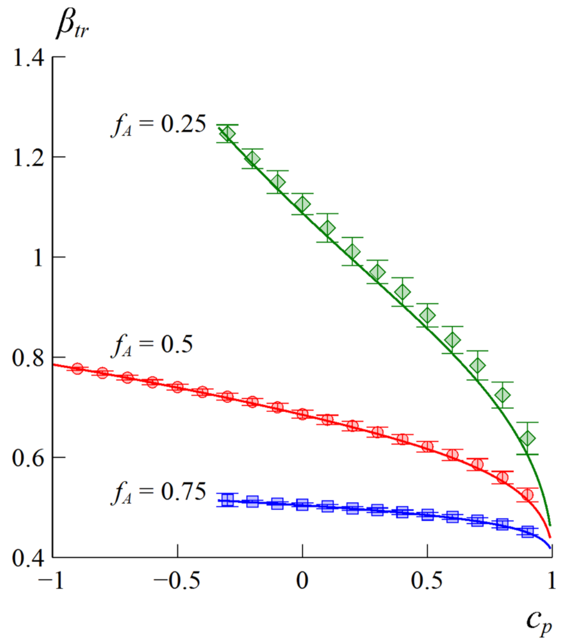

FIG. 9. Inverse transition temperature as a function of the RC correlation parameter c_p for a RC adsorbing onto a homogeneous surface calculated in the annealed approximation (lines) and for RPC (symbols). The A-monomer unit probability in the sequence, f_A, is shown in the plots. Monomer-surface interaction energies are $\epsilon_A = -1$ and $\epsilon_B = 0$.

Correspondingly, the matrix $\mathbf{W}$ is constructed so that it now has the dimension $(m_p m_s) \times (m_p m_s)$ [26]. The advantage of this approach is that the adsorption transition point for each random period realization in the RPC is calculated *exactly*.

Let us first test this idea for the RC adsorption a homogeneous surface. Let the A units be attractive to the surface and B units be neutral. We made calculations for different period lengths m_p and observed that the results approach the theoretical dependences obtained in the annealed approximation as the period length increases. In Fig. 9, we present the results for the largest of the considered lengths $m_p = 4000$. For each pair of f_A and c_p, 100 realizations of the random sequence for the RPC period were generated. The results shown in Fig. 9 demonstrate a very good quantitative agreement with the dependence obtained for the RC in the annealed approximation. The agreement is better for larger content of adsorbed units in the chain f_A.

In a similar way, the transition point for the RC adsorption on an inhomogeneous periodic symmetric surface was calculated (Fig. 10, which is similar to Fig. 2). The length of the period for which a random sequence of monomers was generated according to f_A and c_p was equal to $m_p = 1000$ [since the order of the transition probability matrices in this case becomes equal to $(1000m_s) \times (1000m_s)$, we were forced to take a shorter period length than in the case of the homogeneous surface]. For each pair of f_A and c_p, 100 random sequence realizations were generated.

The data presented in Fig. 10 show that the numerical results are in good quantitative agreement with the annealed approximation, i.e., they reproduce the nonmonotonicity of

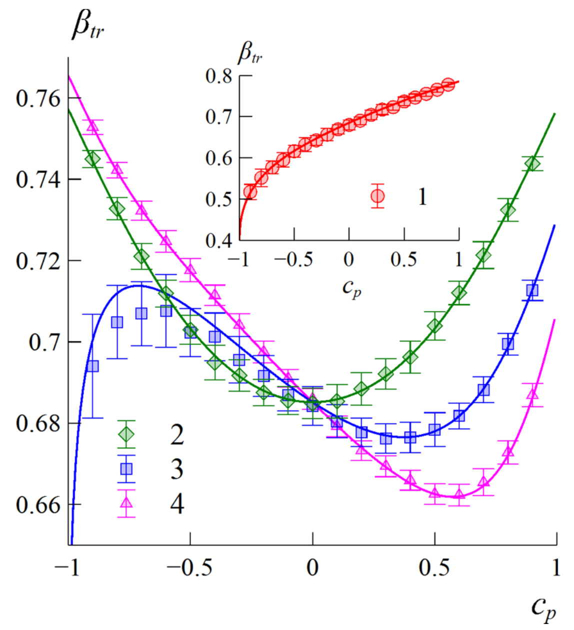

FIG. 10. Inverse transition temperature as a function of the RC correlation parameter c_p for a RC adsorbing onto a symmetric stripe-patterned surface with $\ell_a = \ell_b = 1,2,3,4$, as indicated calculated in the annealed approximation (lines) and for RPC (symbols). The A-monomer unit probability in the sequence $f_A = 0.5$.

the $\beta_{\rm tr}(c_p)$ dependence and the boundary minima at odd ℓ as well.

These results allow us to conclude that the annealed approximation adequately describes the position of the adsorption transition point for the quenched system. A following explanation can be suggested. The transition point corresponds to the equilibrium between the adsorbed and the desorbed states of the macromolecule. In the desorbed state, there are no monomer unit contacts with the surface and no reason to shift the monomer distribution moments from their expected values. In the adsorbed state, at the onset of adsorption, the primary binding of the polymer to the surface occurs via formation of a small number of good contacts, and the choice of these monomer units depends marginally on the finer details of the quenched sequence.

In contrast, for the related problem of localization of a RC at an interface between oil and water, in the delocalized phase all monomer units do contact either oil or water, and this shifts equilibrium towards hydrophobic or hydrophilic units, respectively. Therefore, the moments of the distribution of monomer units are not correct even in the delocalized phase, and application of the annealed approximation gives the incorrect phase diagram. The latter, however, can be substantially improved by application of the Morita approximation [36].

IV. SUMMARY AND CONCLUDING REMARKS

In this work, we studied the adsorption of a RC on a chemically inhomogeneous regular periodic surface. We used the simplest model for solving problems of this kind—the 2D-PDW model of the polymer in two dimensions. The solution was obtained in the framework of the GF method, which was successfully used in the earlier studies of similar systems [24,26] (adsorption of a random copolymer on a random surface and adsorption of a periodic copolymer on a periodic inhomogeneous surface) and the annealed approximation for the averaging over disorder in the RC sequence. For polymers interacting with a chemically inhomogeneous surface, a question naturally arises: Does a polymer exist that adsorbs on the surface with the known pattern, or recognizes this surface pattern, better than the others?

Since the system is multiparametric, we intentionally limited ourselves to studying the adsorption transition point. We found that for a certain class of inhomogeneous surfaces there exists an "optimal" distribution (that is, "optimal" values of the parameters of the random distribution of monomer units in the copolymer) for which the inverse transition temperature has the lowest possible value. The surfaces of this class include compositionally symmetric and "weakly asymmetric" surfaces that only slightly differ from symmetrical ones. On the contrary, if the surface is highly asymmetric, that is, sites of one type prevail, then the best adsorbate is the homopolymer composed of monomers which are complementary to the majority sites on the surface.

This result is remarkable, because for a RC adsorbing onto a *random* surface, such exact matching was not observed, except for the general trend that the surface and the copolymer with the same nature of correlations are better suited to each other.

We also proposed a method for determining the adsorption transition point for a RC with quenched disorder in the infinitely long chain limit by using periodic copolymers with a large period having the RC structure. This approach allowed us to show that the annealed approximation gives a very good quantitative estimate of the adsorption transition point for the RC with quenched disorder.

These results were obtained for the case when the "matching" contacts Aa and Bb were attractive, or energetically favorable, $\epsilon_{Aa} = \epsilon_{Bb} = -1$, while the "mismatching" contacts Ab and Ba were neutral with no energy cost. The choice of interaction parameters has, of course, a significant impact on the system behavior, so we have also carried out calculations for systems with two other "interaction schemes." These results are presented in the Supplemental Material (SM) [40]. The first interaction scheme is a modification of our original scheme with the replacement of neutral Ab and Ba contacts by repulsive contacts with the same strength: $\epsilon_{Ab} = \epsilon_{Ba} = +1$. Figures S1–S7 of the SM demonstrate that the introduction of repulsion into mismatching contacts does not qualitatively change the picture of the behavior of the system, and it affects only the numerical values of the transition point.

The second interaction scheme is $\epsilon_{Aa} = -1$, $\epsilon_{Bb} = \epsilon_{Ab} = \epsilon_{Ba} = 0$, which is simpler than the original one. One can say that there are "stickers" distributed in the polymer and on the surface, of the type A and a, respectively, that attract to each other. Monomer units of the type B do not interact with the surface, and b-sites on the surface neither attract nor repel the RC monomer units. The results for the transition point, Figs. S8 and S9, show that there is no effect of specific "recognition," that is, no local, nonboundary minimum of $\beta_{\rm tr}$. In the symmetric case, if the RC composition is kept constant and equal to $f_A = 0.5$, then the lowest inverse transition temperature will correspond to $c_p = 1$, that is, to the diblock copolymer (or to the multiblock copolymer with very long A and B blocks). There are additional "model-specific" boundary minima at $c_p = -1$ for odd ℓ as well. If the composition is not fixed, then the smallest value of β_{tr} corresponds to the boundary $f_A = 1$, that is, to the homopolymer A.

Thus, we can conclude that for implementation of the "molecular recognition" between a RC and a heterogeneous surface, one pair of Aa of attractive contacts is not enough; there should be at least a second pair. This result suggests the way for further development of the present work. One of the interesting steps in the development of this work would be increasing the number of types of units and sites. If the RC and the inhomogeneous surface were described as Markov chains with an appropriate number of states (more than two), this would not affect the method used in our study.

Another direction of development of this work is to go beyond the transition point and to investigate the temperature dependences of the main characteristics of the RC chain interacting with the surface—of course, taking into account the results of the present study.

ACKNOWLEDGMENTS

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