Polymer Chain Adsorption on a Solid Surface: Scaling Arguments and Computer Simulations

A. Milchev\textsuperscript{1,2}, V. Rostiashvili\textsuperscript{2}, S. Bhattacharya\textsuperscript{2} and T. Vilgis\textsuperscript{2}

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria, milchev@ipc.bas.bg and Max Planck Institute for Polymer Research, 10 Ackermannweg 55128 Mainz, Germany

We examine the phase transition of polymer adsorption as well as the underlying kinetics of polymer binding from dilute solutions on a structureless solid surface. The emphasis is put on the properties of regular multiblock copolymers, characterized by block size $M$ and total length $N$ as well as on random copolymers with quenched composition $p$ of sticky and neutral segments. The macromolecules are modeled as coarse-grained bead-spring chains subject to a short-ranged surface adhesive potential. Phase diagrams, showing the variation of the critical threshold for single chain adsorption in terms of $M$ and $p$ are derived from scaling considerations in agreement with results from computer experiment.

Using both scaling analysis and numerical data from solving a system of coupled Master equations, we demonstrate that the phase behavior at criticality, and the adsorption kinetics may be accurately predicted and understood, in agreement with the results of extensive Monte Carlo simulations. Derived analytic expressions for the mean fraction of adsorbed segments as well as for probability Distribution Functions of the various structural building blocks (i.e., trains, loops, tails) at time $t$ during the chain attachment process are in good agreement with our numeric experiments and provide insight into the mechanism of polymer adsorption.

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I. INTRODUCTION

The adsorption of polymers on solid surfaces is a long-standing problem which plays an important role in a number of applications in technology (protective coatings, adhesives, lubricants, stabilization of colloids, flocculation, etc.) and biology (adsorption of biopolymers, etc.). As a phenomenon it poses a number of challenging scientific problems too. Important theoretical contributions have been made by Birshtein\textsuperscript{5}, de Gennes\textsuperscript{6}, Eisenriegler et al.\textsuperscript{7}. Later studies have covered adsorption of polyelectrolytes\textsuperscript{8}, dynamics of adsorbed chains\textsuperscript{9}, and adsorption on chemically heterogeneous surfaces\textsuperscript{10}. The close relationship between analytic theory and computer experiments in this field\textsuperscript{10,11,12,13,14} has proved especially fruitful and instructive.

While the investigations mentioned above have been devoted exclusively to homopolymers, the adsorption of copolymers (e.g., random or multi-blocks copolymers) still poses open questions. Thus, for instance, the critical adsorption potential (CAP) dependence on block size $M$ at fixed concentration of the sticking $A$-monomers is still unknown as are the scaling properties of regular multi-block copolymers in the vicinity of the CAP. From the theoretical perspective, the case of diblock copolymers has been studied by means of the Grand Canonical Ensemble (GCE)-approach\textsuperscript{15,16}, within the Self-Consistent Field (SCF)-approach\textsuperscript{17,18}, or by Monte Carlo computer simulations\textsuperscript{19,20}. The case of random copolymers adsorption has gained comparatively more attention by researcher so far. It has been investigated by Whittington et al.\textsuperscript{21,22} using both the annealed and quenched models of randomness. The influence of sequence correlations on the adsorption of random copolymers has been treated by means of the variational replica method approach\textsuperscript{22}. Sumithra and Baumgaertner\textsuperscript{23} examined the question of how the critical behavior of random copolymer differs from that of homopolymers. Thus, among a number of important conclusions, the results of Monte Carlo simulations demonstrated that the so called adsorption (or, crossover) exponent $\phi$ (see below) is independent of the fraction of attractive monomers $n$.

The adsorption kinetics of polymers has been intensively studied both experimentally\textsuperscript{24,25} and theoretically\textsuperscript{26,27,28,29,30,31,32,33} since more than two decades now. A key parameter thereby is the height of the free energy adsorption barrier that the polymer chain has to overcome so as to bind to the surface. High barriers are usually referred to as cases of chemisorption as opposed to those of physisorption which are characterized by low barriers for adsorption. Depending on the strength of the binding interaction $\epsilon$, one distinguishes then between weak physisorption when $\epsilon$ is of the order of the thermal energy $k_B T$ (with $k_B$ being the Boltzmann constant), and strong physisorption when $\epsilon \geq 2k_B T$. One of the important questions concerns the scaling of the adsorption time $\tau_{ads}$ with the length of the polymer chain $N$ in dilute solutions. For homopolymers in the regime of strong physisorption (that is, for sticking energy considerably above the CAP) computer experiments\textsuperscript{28,31,32} suggest $\tau_{ads} \propto N^\alpha$ where $\alpha$ is related to the Flory exponent $\nu$ as $\alpha = 1 + \nu \approx 1.59$. This result follows from the assumed zipping mechanism in the absence of a significant barrier whereby the chain adsorbs predominantly by means of sequential, consecutive attachment of monomers, a process that quickly erases existing loops on the substrate. For the case of weak adsorption, one should
mention a recent study \cite{33}, where one finds in contrast \( \alpha = (1 + 2\nu)/(1 + \nu) \approx 1.37 \) which suggests shorter time scale for surface attachment. In chemisorption, the high barrier which attaching monomers encounter slows down the binding to the surface, the chain gains more time to attain equilibrium conformation and the adsorption process is believed to involve large loop formation giving rise to accelerated zipping mechanism \cite{29,30}. The predicted value of \( \alpha \) in agreement with MC results is \( \alpha \approx 0.8 \pm 0.02 \) \cite{32}. A comprehensive overview of experimental work and theoretic considerations may be found in the recent review of O’Shaughnessy and Vayylonis \cite{30}.

In the present contribution we focus on copolymer physisorption, extending thus the aforementioned studies of homopolymers statics and kinetics. We show how scaling analysis as well as different MC-simulation methods help understand the critical behavior of multi-block and random copolymers. It turns out that the critical behaviour of these two types of copolymers can be reduced to the behavior of an effective homopolymer chain with "renormalized" segments. For multi-block copolymers one can thus explain how the adsorption threshold depends on the block length \( M \) and even derive an adsorption phase diagram in terms of CAP against \( M \). In the case of random copolymers, the sequence of sticky and neutral (as regards the solid substrate) monomers within a particular chain is usually fixed which exemplifies a system with quenched randomness. Nevertheless, close to criticality the chain is still rather mobile, so that the sequence dependence is effectively averaged over the time of the experiment and the problem can be reduced to the easier case of annealed randomness. We show that the MC-findings close to criticality could be perfectly described within the annealed randomness model.

For both regular multiblock as well as for random copolymers, we compare the predicted kinetics of adsorption in the regime of strong physisorption, to consistent numeric data derived from simulations and coupled Master equations. We demonstrate that the observed adsorption kinetics is close to that of homopolymers and suggest interpretation of typical deviations. Eventually, we should like to stress that the complex polymer hydrodynamics near an interface has remained beyond the scope of this paper.

\section{II. Simulation Methods}

Apart from the frequently used Bond-Fluctuation Method (BFM) \cite{28,32}, two coarse-grained models, a bead-spring off-lattice model \cite{9} and a cubic lattice model implementing the so called pruned-enriched Rosenbluth method (PERM) \cite{14}, are used to test theoretical predictions.

\subsection{A. Off-lattice bead-spring model}

In our computer simulations we use a coarse grained off-lattice bead spring model\cite{11} to describe polymer chains. The system consists of a single chain tethered at one end to a flat structureless surface so as to avoid problems with translational entropy depending on the box size. There are two kinds of monomers: "A" and "B", of which only the "A" type feels an attraction to the surface. The surface interaction of the "A" type monomers is described by a short-range square well potential \( U_w(z) = \epsilon \) for \( z < \delta \) and \( U_w(z) = 0 \) otherwise, whereby the range \( \delta = 0.125 \) (in units of the maximal bond length extension \( l_{\text{max}} \) between adjacent beads). The effective bonded interaction is described by the FENE (finitely extensible nonlinear elastic) potential.

\begin{equation}
U_{\text{FENE}} = -K(1 - l_0)^2 \ln \left[ 1 - \left( \frac{l - l_0}{l_{\text{max}} - l_0} \right)^2 \right]
\end{equation}

with \( K = 20, l_{\text{max}} = 1, l_0 = 0.7, l_{\text{min}} = 0.4 \).

The nonbonded interactions are described by the Morse potential.

\begin{equation}
\frac{U_I(r)}{\epsilon_I} = \exp(-2\alpha(r - r_{\text{min}})) - 2 \exp(-\alpha(r - r_{\text{min}}))
\end{equation}

with \( \alpha = 24, r_{\text{min}} = 0.8, \epsilon_I/k_BT = 1 \).

We use periodic boundary conditions in the \( x - y \) directions and impenetrable walls in the \( z \) direction. We study homopolymer chains, regular multiblock copolymers, and random copolymers (with a fraction of attractive monomers, \( p = 0.25, 0.5, 0.75 \)) of length 32, 64, 128, 256 and 512. The size of the box is \( 64 \times 64 \times 64 \) in all cases except for the 512 chains where we use a larger box size of \( 128 \times 128 \times 128 \). The standard Metropolis algorithm is employed to govern the moves with self avoidance automatically incorporated in the potentials. In each Monte Carlo update, a monomer is chosen at random and a random displacement attempted with \( \Delta x, \Delta y, \Delta z \) chosen uniformly from the interval \(-0.5 \leq \Delta x, \Delta y, \Delta z \leq 0.5 \). The transition probability for the attempted move is calculated from the change \( \Delta U \) of
the potential energies before and after the move as \( W = \exp(-\Delta U/k_B T) \). As for a standard Metropolis algorithm, the attempted move is accepted if \( W \) exceeds a random number uniformly distributed in the interval \([0, 1)\).

Typically, the polymer chains are originally equilibrated in the MC method for a period of about \( 10^6 \) MCS (depending on degree of adsorption \( \epsilon \) and chain length \( N \) this period is varied) whereupon one performs 200 measurement runs, each of length \( 8 \times 10^6 \) MCS. In the case of random copolymers, for a given composition, i.e., percentage \( p \) of the \( A \)--monomers, we create a new polymer chain in the beginning of the simulation run by means of a randomly chosen sequence of segments. This chain is then sampled during the course of the run, and replaced by a new sequence in the beginning of the next run.

![FIG. 1: Schematic representation of a grafted chain close to criticality. Snapshot of a regular multiblock copolymer with length \( N = 2048 \) and block size \( M = 8 \) from the PERM simulation.](image)

**B. Coarse-grained lattice model with PERM**

The adsorption of a diblock \( AB \) copolymer with one end (monomer \( A \)) grafted to a flat impenetrable surface and with only the \( A \) monomers attractive to the surface is described by self-avoiding walks (SAW) of \( N-1 \) steps on a simple cubic lattice with restriction \( z \geq 0 \). The partition sum may be written as

\[
Z_N^{(1)}(q) = \sum_{N_s} A_N(N_s) q^{N_s}
\]

where \( A_N(N_s) \) is the number of configurations of SAWs with \( N \) steps having \( N_s \) sites on the wall, and \( q = e^{\epsilon/k_B T} \) is the Boltzmann factor (\( \epsilon > 0 \) is the attractive energy between the monomer \( A \) and the wall). Clearly, any copolymer will collapse onto the wall, if \( q \) becomes sufficiently large. Therefore one expects a phase transition from a grafted but otherwise detached phase into an adsorbed phase, similar to the transition observed for homopolymers.

The pruned-enriched Rosenbluth method (PERM) [14], also used in our simulations, is a biased chain growth algorithm with resampling ("population control") and depth-first implementation. Polymer chains are built like random walks by adding one monomer at each step. Thus the total weight of a configuration for a polymer consisting of \( N \) monomers is a product of those weight gains at each step, i.e., \( W_N = \prod_{i=0}^{N-1} w_i \). As in any such algorithm, there is a wide range of possible distributions of sampling so we have the freedom to give a bias at each step while the chain grows, and the bias is corrected by means of giving a weight to each sample configuration, namely, \( w_i \to w_i/p_i \) where \( p_i \) is the probability for putting the monomer at step \( i \). In order to suppress the fluctuations of weights as the chain is growing, the population control is done by "pruning" configurations with too low weight and "enriching" the sample with copies of high-weight configurations. Therefore, two thresholds are introduced here, \( W^+_n = c^+ Z_n \) and \( W^-_n = c^- Z_n \), where \( Z_n = \frac{1}{N_{config}} \sum_{config} W_n \) from the \( M_n \) trail configuration is the current estimate of partition sum at the \( n-1 \) step, \( c^+ \) and \( c^- \) are constants of order unity and \( c^+/c^- \approx 10 \). In order to compare with the results obtained by the first MC method, we simulate homopolymers of length \( N = 2048 \) and multi-block copolymers with block size \( M = 2^k \), \( k = 0, 1, 2, \cdots, 9 \) (see Fig. [1]). The number of monomers is increased to \( N = 8192 \) as the block size increases. There are \( 10^5 \div 10^6 \) independent configurations for each measurement. We also simulate random copolymers of \( N = 2048 \) monomers with composition \( p = 0.125, 0.25, 0.50, \) and \( 0.75 \).
III. SCALING BEHAVIOR AT CRITICALITY

A. A homopolymer chain

It is well known that a single polymer chain undergoes a transition from a non-bound into an adsorbed state when the adsorption energy $\epsilon$ per monomer increases beyond a critical value $\epsilon_c \approx k_BT$ (where $T$ stands for the temperature of the system). The adsorption transition can be interpreted as a second-order phase transition at the critical point (CAP) of adsorption $\epsilon = \epsilon_c$, in the thermodynamical limit, i.e., $N \to \infty$. Close to the CAP the number of surface contacts $N_s$ scales as $N_s(\epsilon = \epsilon_c) \sim N^\phi$. The numerical value of $\phi$ is somewhat controversial and lies in a range between $\phi = 0.59$ (ref. 7) and $\phi = 0.484$ (ref. 14), we adopt however the value $\phi = 0.50 \pm 0.02$ which has been suggested as the most satisfactory by comparison with comprehensive simulation results.

How does polymer structure vary with adsorption strength? Consider a chain tethered to the surface at the one end. The fraction of monomers on the surface $n = N_s/N$ may be viewed as an order parameter measuring the degree of adsorption. In the thermodynamic limit $N \to \infty$, the fraction $n$ goes to zero ($\approx O(1/N)$) for $\epsilon \ll \epsilon_c$, then near $\epsilon_c$, $n \sim N^{\phi-1}$ whereas for $\epsilon \gg \epsilon_c$ (in the strong coupling limit) $n$ is independent of $N$. Let us measure the distance from the CAP by the dimensionless quantity $\kappa = (\epsilon - \epsilon_c)/\epsilon_c$ and also introduce the scaling variable $\eta \equiv \kappa N^\phi$. The corresponding scaling ansatz [32] is then $n(\eta) = N^{\phi-1} G(\eta)$ with the scaling function

$$G(\eta) = \begin{cases} \text{const} & \text{for } \eta \rightarrow 0 \\ \eta^{(1-\phi)/\phi} & \text{for } \eta \gg 1 \end{cases}$$

(3.1)

The resulting scaling behavior of $n$ follows as,

$$n \propto \begin{cases} 1/N & \text{for } \kappa \ll 0 \\ N^{\phi-1} & \text{for } \kappa \rightarrow 0 \\ \kappa^{(1-\phi)/\phi} & \text{for } \kappa \gg 1 \end{cases}$$

(3.2)

The gyration radius in direction perpendicular to the surface, $R_{g\perp}(\eta)$, has the form $R_{g\perp}(\eta) = a N^{\nu} G_{g\perp}(\eta)$. One may determine the form of the scaling function $G_{g\perp}(\eta)$ from the fact that for $\kappa < 0$ one has $R_{g\perp} \sim N^{\nu}$ so that $G_{g\perp} = \text{const}$. In the opposite limit, $\eta \gg 0$ the $N$-dependence drops out and $G_{g\perp}(\eta) \sim \eta^{-\nu/\phi}$.  In result

$$R_{g\perp}(\eta) \propto \begin{cases} a N^{\nu} & \text{for } \eta \leq 0 \\ \kappa^{-\nu/\phi} & \text{for } \eta \gg 0 \end{cases}$$

(3.3)

The gyration radius in direction parallel to the surface has similar scaling representation, $R_{g\parallel}(\eta) = a N^{\nu} G_{g\parallel}(\eta)$. Again at $\kappa < 0$ the gyration radius $R_{g\parallel} \sim a N^{\nu}$ and $G_{g\parallel} = \text{const}$. At $\eta \gg 0$ the chain behaves as a two-dimensional self-avoiding walk (SAW), i.e., $R_{g\parallel} \sim a N^{\nu_2}$, where $\nu_2 = 3/4$ denotes the Flory exponent in two dimensions. In result, the scaling function behaves as $G_{g\parallel}(\eta) = \eta^{(\nu_2 - \nu)/\phi}$, at $\eta \gg 0$. Thus

$$R_{g\parallel}(\eta) \propto \begin{cases} a N^{\nu} & \text{at } \eta \leq 0 \\ \kappa^{(\nu_2 - \nu)/\phi} N^{\nu_2} & \text{at } \eta \gg 0 \end{cases}$$

(3.4)

The study of the ratio $r(\eta) \equiv R_{g\perp}/R_{g\parallel}$ of gyration radius components is a convenient way to find the value of $\epsilon_c$. In fact, from the previous scaling equations $r(\eta) = G_{g\perp}(\eta)/G_{g\parallel}(\eta)$. Hence at the CAP, i.e., at $\eta \rightarrow 0$ the ratio $r(0) = \text{const.}$ is independent of $N$. Thus, by plotting $r$ vs. $\epsilon$ for different $N$ all such curves should intersect at a single point which gives $\epsilon_c$ - cf. Fig. 4.

If the well-known picture of blobs is invoked, then in the limit $\kappa N^\phi \gg 1$ the adsorbed chain can be visualized as a string of adsorption blobs which forms a pancake-like quasi-two-dimensional layer on the surface. The blobs are defined to contain as many monomers $g$ as necessary to be on the verge of being adsorbed and therefore carry an adsorption energy of the order of $k_BT g$ each. The thickness of the pancake $R_{g\perp}$ corresponds to the size of the blob while the chain conformation within a blob stays unperturbed (i.e., it is simply a SAW), therefore $g \sim (R_{g\perp}/a)^{1/\nu} = \kappa^{-1/\phi}$ where we have used Eq. 3.3. The gyration radius can be represented thus as

$$R_{g\parallel} = R_{g\perp} \left( \frac{N}{g} \right)^{\nu_2} \propto \kappa^{(\nu_2 - \nu)/\phi} N^{\nu_2}$$

(3.5)

and one goes back to Eq. 3.4 which proves the consistency of the adsorption blob picture. Generally speaking, the number of blobs, $N/g \sim \kappa^{1/\phi} N$, is essential for the main scaling argument in the above-mentioned scaling functions.
The adsorption on a plane at $\kappa > 0$ is due to free energy gain which is then proportional to the number of blobs, i.e.,

$$F - F_{\text{bulk}} \propto -N / g \sim -\kappa^{1/\phi} N.$$  

The expression for the specific heat per monomer may be then obtained as

$$C_V = -\frac{\partial^2 (F - F_{\text{bulk}})}{\partial \kappa^2} \propto \kappa^{-\alpha},$$  

where $\alpha = 2 - \phi^{-1}$. If $\phi = 0.5$ then $\alpha = 0$ and the specific heat does not diverge but rather undergoes a jump at the CAP - cf. Fig. 2(b).

**B. Multiblock Copolymer Adsorption**

One may now consider the adsorption of a regular multi-block copolymer comprising monomers $A$ which attract (stick) to the substrate and monomers $B$ which are neutral to the substrate. In order to treat the adsorption of a regular multi-block $AB$-copolymer it may be reduced to that of a homopolymer which has been considered above. Thus a regular multi-block copolymer can be treated as an “homopolymer” where a single $AB$-diblock plays the role of an effective monomer $\gamma_c$. Let each individual diblock consist of an attractive $A$-block of length $M$ and a neutral $B$-block of the same length. Upon adsorption, the $A$-block would form a string of blobs whereas the $B$-part forms a non-adsorbed loop or a tail. The free energy gain of the attractive block may be written then (in units of $k_B T$) as

$$F_{\text{attr}} = -\kappa^{1/\phi} M$$  

where $\kappa \equiv (\epsilon - \epsilon_c^b) / \epsilon_c^h$ now measures the normalized distance from the CAP $\epsilon_c^h$ of a homopolymer. The neutral $B$-part which is most frequently a loop connecting adjacent $A$-blocks, but could also be a tail with the one end free, contributes only to the entropy loss $F_{\text{rep}} = (\gamma - \gamma_1) \ln M$ where the universal exponents $\gamma$ and $\gamma_1$ are well known $\gamma_1 = 0.679$ (e.g. in 3D - space $\gamma = 1.159$, $\gamma_1 = -0.390$). If a tail is involved, one should also use the exponent $\gamma_1 = 0.679$ albeit this does not change qualitatively the expression for $F_{\text{rep}}$. These expressions reflect the standard partition functions for a free chain, a chain with both ends fixed at a two points, and for a chain, tethered by the one end $\gamma_1 = 0.679$. In result the effective adsorption energy of a diblock is $\gamma_c^M$:

$$E(M) = \kappa^{1/\phi} M - (\gamma - \gamma_1) \ln M.$$  

One can tackle the problem of regular copolymer adsorption by mapping it on that of a “homopolymer”, consisting of $\mathcal{N} = N / 2M$ such effective units by using $a \rightarrow a M^n$, $\kappa \rightarrow \Delta = \frac{E - E_c^b}{\epsilon_c^b}$, $N \rightarrow \mathcal{N}$ where $a$ denotes the monomer size, and $E_c^b$ is the critical adsorption energy of the renormalized homopolymer. Generally, one would expect $E_c^b$ to be of the order of $\epsilon_c^b$, reflecting the model dependence of the latter. At the CAP of the multiblock chain one has $\Delta = 0$, thus one can estimate the deviation $\kappa_c^M$, of the corresponding critical energy of adsorption, $\epsilon_c^M$, from that of a homopolymer, namely

$$\kappa_c^M \equiv \frac{\epsilon_c^M - \epsilon_c^b}{\epsilon_c^b} = \left( \frac{(\gamma - \gamma_1) \ln M + E_c^b}{M} \right)^{\phi}. $$  

**FIG. 2:** Variation of the ratio $R_{gL}^2 / R_{g||}^2$ for a copolymer of block size $M = 2$ (a), and of the specific heat per monomer, $C_V / N$ for a homopolymer (b) with surface energy $\epsilon$ for different chain length $N$. One gets $\epsilon_c^M = 0.556$ and $\epsilon_c^b = 0.284$ (PERM).
where we have used Eq. 3.7. It is seen from the phase diagram, Fig. 3a, that the deviation
\[ n \propto N^{q-1} G \left( \frac{N}{M^q} \right) \] (3.9)
For sufficiently strong adsorption, \( \kappa \sqrt{M} \gg 1 \) and \( \Delta \sqrt{N/M} \gg 1 \), one gets thus \( n \propto \kappa \Delta \).

The gyration radius component in direction perpendicular to the surface \( R_{g\perp} = a N^\nu \left( \Delta \left( \frac{N}{M^q} \right) \right) \) becomes
\[ R_{g\perp} \approx a M^\nu \left( \frac{E^b}{M^q} \right)^{2\nu} \] (3.10)
In a similar manner, the gyration radius component parallel to the surface has the form \( R_{g\parallel} = a N^\nu \left( \Delta \left( \frac{N}{M^q} \right) \right) \)
which in the limit \( \Delta \sqrt{N/M} \gg 1 \) results in \( R_{g\parallel} \approx a \left( \frac{\Delta^{1/q}}{M^{q/2-\nu}} \right) N^{\nu/2} \), i.e.,
\[ R_{g\parallel} \approx a \left[ \frac{\Delta^{1/q}}{M^{q/2-\nu}} \right] \left( \frac{M^{q/2-\nu}}{M^{q/2-\nu}} \right) N^{\nu/2} \] (3.11)
As shown in Fig. 4, one finds indeed the expected scaling behavior which is demonstrated by the collapse of the simulation data on few “master curves”, absorbing cases of different strength of adsorption \( \kappa \). Like in the homopolymer case, one can define a blob length \( G \sim \left( R_{g\perp} / a \right)^{1/\nu} \sim \Delta^{-1/q} M \) which in the strong adsorption limit, \( \Delta \geq 1 \), approaches the block length, \( G \approx M \), as it should be.

C. Random Copolymer Adsorption

The adsorption of a random copolymer on a homogeneous surface has been studied by Whittington et al. [21, 22] within the framework of the annealed disorder approximation. Physically this means that during the measurements
the chain touches the substrate at random in such a way that one samples all possible monomers sequences along the backbone of the macromolecule. Following this assumption \cite{21}, let $c_N(n)$ be the number of polymer configurations such that $n$ units have contact with the surface simultaneously. The percentage of $A$-monomers (composition) is denoted by $p$. In the annealed approximation one then averages the partition function over the disorder distribution, i.e.,

$$Z(\epsilon) = \sum_{n=1}^{N} \sum_{n_p=0}^{n} c_N(n) \binom{n}{n_p} p^{n_p}(1-p)^{n-n_p} e^{\epsilon n_p}$$

$$= \sum_{n=1}^{N} c_N(n) (pe^\epsilon + 1 - p)^n = \sum_{n=1}^{N} c_N(n) e^{\epsilon n} e^{-\epsilon n}$$

(3.12)

where $e_{c}^{h}$ is the attraction energy of an effective homopolymer. From Eq. 3.12 one can see that the annealed problem is reduced to that of a homopolymer where the effective attractive energy is defined as $e_{c}^{h} = \ln [pe^\epsilon + 1 - p]$. Since the homopolymer attraction energy at the CAP is $e_{c}^{h} = e_{c}^{c}$, the critical attraction energy $\epsilon = e_{c}^{c}$ of a random copolymer will be

$$e_{c}^{p} = \ln \left[ \exp e_{c}^{h} + p - 1 \right] \geq e_{c}^{h}$$

(3.13)

where the composition $0 \leq p \leq 1$. At $p \to 0 e_{c}^{p} \to \infty$ whereas at $p = 1 e_{c}^{p} = e_{c}^{h}$. This prediction which has been recently confirmed by Monte Carlo simulations \cite{37}, is plotted in Fig. 3b. It shows that close to criticality the chain is still rather mobile, so that the sequence dependence is effectively averaged over the time of the experiment and the of quenched disorder can be reduced to that of annealed randomness.

IV. ADSORPTION KINETICS

A. Variation of the adsorbed fraction with elapsed time - Theory

We illustrate here how one can use the “stem - flower” notion of adsorbing linear macromolecule, suggested by Descas et al. \cite{31}, to describe the observed “zipping” dynamics \cite{32} of adsorption not only in terms of the average fraction of adsorbed segments but to include also time-dependent train and tail distribution functions as main constituents of the dynamic adsorption theory. The simple “zipping” mechanism along with the underlying stem-flower model are illustrated in Fig. 5a,b. The number of the adsorbed monomers at time $t$ is denoted by $n(t)$. The nonadsorbed fraction of the chain is subdivided into two parts: a stretched part (“stem”) of length $m(t)$, and a remaining part (“flower”) which is yet not affected by the tensile force of the substrate. The tensile force propagation front is at distance $R(t)$ from the surface. The rate of adsorption is denoted as $v(t) = \frac{dn(t)}{dt}$, where $a$ is the chain segment length.
A single adsorption event occurs with energy gain $\epsilon$ and entropy loss $\ln(\mu_3/\mu_2)$, where $\mu_3$ and $\mu_2$ are the connectivity constants in three and two dimensions, respectively [36], so that the driving free energy $F_{dr} = \epsilon - k_B T \ln(\mu_3/\mu_2)$ whereas the driving force $f_{dr} = F_{dr}/a$. The friction force is related to the pulling of the stem at rate $v(t)$, i.e., $f_{fr} = \zeta_0 a m(t) \frac{dn(t)}{dt}$ where $\zeta_0$ is the Stokes friction coefficient of a single bead. The equation of motion, following from the balance of driving, and drag force, is then $f_{dr} = f_{fr}$. Inspection of Fig. 4A suggests that the distance $R(t)$ between the flower and the plane changes during the adsorption process until the flower is eventually “consumed”. In so doing $R(t)$ obeys two relationships: $R(t) \approx a[n(t) + m(t)]$ (because it is actually the size which the chain portion $n(t) + m(t)$ occupied before the adsorption has started) and $R(t) \approx m(t)$ (up to a geometric factor of order unity). Thus $n(t) \approx m(t)^{1/\nu} - m(t)$ which yields $m(t) \approx n(t)^{\nu}$ for the typically long stems $m(t) \gg 1$. From the resulting equation $\zeta_0 n(t)^{\nu} \frac{dn(t)}{dt} = f_{dr}/a^2$ then follows $n(t) \propto t^{1/(1+\nu)} \approx t^{0.62}$ which is in good agreement with simulation results [28, 31, 52].

B. Time evolution of the distribution functions - Theory

Consider the instantaneous number of adsorbed monomers $n$ at time $t$, i.e., the total train length, distribution function $P(n,t)$. Using the ‘Master Equation’ method [38], one may derive a system of coupled kinetic equations for $P(n,t)$ by treating the zipping dynamics as a one step adsorption / desorption process within an elementary time interval. Assuming that the corresponding rate constants $w^+(n)$, $w^-(n)$ of monomer attachment / detachment are related by the detailed balance condition [38] (which is an approximation for a non-equilibrium process), one can fix their ratio $w^+(n-1)/w^-(n) = \exp(F_{dr}/k_B T)$, and even fully specify them by introducing a friction-dependent transmission coefficient $q(m) = k_B T/(a^2 \zeta_0 m)$ (whereby the stem length $m$ depends on the total train length $n$, according to $n \approx m^{1/\nu} - m$). Then the one-step Master Equation reads [38]

$$\frac{d}{dt} P(n,t) = w^-(n+1) P(n+1,t) + w^+(n-1) P(n-1,t) - w^+(n) P(n,t) - w^-(n) P(n,t),$$

which along with the boundary conditions

$$\frac{d}{dt} P(1,t) = w^-(2) P(2,t) - w^+(1) P(1,t), \quad \text{for } n = 1$$

$$\frac{d}{dt} P(N,t) = w^+(N-1) P(N-1,t) - w^-(N) P(N,t), \quad \text{for } n = N$$

and $P(n,t = 0) = \delta(n-1)$ fully describe the single chain adsorption kinetics.

![Diagram](image_url)
The equation of motion for the mean number of adsorbed segments \( \langle n \rangle = \sum_{n=1}^{\infty} nP(n,t) \), can be obtained from Eq. (4.1), assuming for simplicity \( P(N,t) = P(0,t) = 0 \):

\[
\frac{d}{dt} \langle n \rangle = -\langle w^-(n) \rangle + \langle w^+(n) \rangle
\]

(4.3)

With the relations for the rate constants, \( w^+(n), w^-(n) \), this equation of motion becomes

\[
\zeta_0 m(t) \frac{d}{dt} n(t) = \frac{k_B T}{\alpha^2} \left[ 1 - e^{-F_{dr}/k_B T} \right]
\]

(4.4)

where for brevity we use the notations \( n(t) = \langle n \rangle \) and \( m(t) = \langle m \rangle \). Note that Eq. (4.4) reduces to the kinetic equation [31], derived at the end of Section IV A for weak driving force, \( F_{dr} \ll k_B T \), by neglecting fluctuations in the zipping mechanism. Evidently, by taking fluctuations into account, \( F_{dr}/a \) is replaced by a kind of effective second virial coefficient \((k_B T/a)(1 - \exp(-F_{dr}/k_B T))\). Thus, the zipping as a strongly non-equilibrium process cannot be treated quasistatically by making use of a simple “force balance”.

C. Order parameter adsorption kinetics - MC results

The time variation of the order parameter \( n(t)/N \) (the fraction of adsorbed segments) for homopolymer chains of different length \( N \) and strong adhesion \( \epsilon/k_B T = 4.0 \) is shown in Fig. 6a,b whereby the observed straight lines in double-log coordinates suggest that the time evolution of the adsorption process is governed by a power law. As the chain length \( N \) is increased, the slope of the curves grows steadily, and for length \( N = 256 \) it is equal to \( \approx 0.56 \). This value is close to the theoretically expected slope of \((1 + \nu)^{-1} \approx 0.62 \). The total time \( \tau \) it takes a polymer chain to be fully adsorbed is found to scale with chain length as \( \tau \propto N^{\alpha} \) whereby the observed power \( \alpha \approx 1.51 \) is again somewhat smaller than the expected one \( 1 + \nu \approx 1.59 \), most probably due to finite-size effects. One may also verify from Fig. 6b that for a given length \( N \) the final (equilibrium) values of the transients at late times \( t \to \infty \) grow while the curves are horizontally shifted to shorter times as the surface potential gets stronger. Nonetheless, the slope of the \( n(t) \) curves remains unchanged when \( \epsilon/k_B T \) is varied, suggesting that the kinetics of the process is well described by the assumed zipping mechanism. The changing plateau height may readily be understood as reflecting the correction in the equilibrium fraction of adsorbed monomers due to the presence of defects (vacancies) for any given value of \( \epsilon/k_B T \). For the transients which collapse on a master curve, cf. the second inset in Fig. 6b, one may view the rescaling of the time axis by the expression \( t \to t[1 - 13.7 \exp(-\epsilon/k_B T)] \) as a direct confirmation of Eq. (4.4) where the time variable
The initial "shoulder", is shown in the upper left inset. The lower inset displays the variation of the scaling exponent, sufficiently large blocks one would therefore expect that this time interval, the temporal length of this shoulder reflects the time it takes for a segment from the polymer chain to be captured by the attractive surface, once the first adsorption \(\tau\) is interrupted by neutral monomers. The characteristic shoulder in the adsorption transients of regular multiblock copolymers manifests itself in the early stage of adsorption and lasts progressively longer when \(N\) grows. The temporal length of this shoulder reflects the time it takes for a segment from the second adsorptive A-block in the polymer chain to be captured by the attractive surface, once the first A-block has been entirely adsorbed. For sufficiently large blocks one would therefore expect that this time interval, \(\tau_1\), associated with the capture event, will scale as the Rouse time, \(M^{-1+2\nu}\), of a non-adsorbing tethered chain of length \(M\). The observed \(\tau_1\) versus \(M\) relationship has been shown in the upper left inset in Fig. 7a. The slope of \(\approx 1.49\) is less that the Rouse time scaling exponent, 2.18, which one may attribute to the rather small values of the block length \(M\) that were accessible in our simulation. One should also allow for scatter in the end time of the shoulder due to the mismatch in the capture times of all the successive A-blocks in the course of our statistical averaging over many chains during the computer experiment.

Somewhat surprisingly, \(\alpha\) which describes the scaling of the total adsorption time with polymer size, \(\tau \propto N^\alpha\), is observed to decline as the block size \(M\) is increased - in contrast to the general trend of regular multiblock copolymers which resemble more and more homopolymers (where \(\alpha = 1 + \nu\)), as the block size \(M \to \infty\). Evidently, the frequent disruption of the zipping process for smaller blocks \(M\) slows down the overall adsorption.

In the case of random copolymers, Fig. 7b, the transients resemble largely those of a homopolymer chain with the same number of beads again, apart from the expected difference in the plateau height which is determined by the equilibrium number of adsorbed monomers. A rescaling of the vertical axis with the fraction of sticking monomers, \(p\), however, does not lead to coinciding plateau heights - evidently the loops, whose size also depends on \(p\), affect the equilibrium number of adsorbed monomers. The variation of the observed scaling exponent \(\alpha\) with composition \(p\) is shown in the inset to Fig. 7b wherefrom one gets \(\alpha \approx 1.6\) with \(\alpha\) being largely independent of \(p\). Note that this value is considerably lower than the power of 2.24 which has been observed earlier \[28\], however, for very short chains with only 10 sticking beads. One may conclude that even for random copolymer adsorption the typical time of the process scales as \(\tau \propto N^\alpha\), as observed for homo- and regular block copolymers. It is conceivable, therefore, that an effective zipping mechanism in terms of renormalized segments, that is, segments consisting of an A and B diblock unit of length \(2M\) for regular multiblock copolymers provides an adequate notion of the way the adsorption kinetics may be

FIG. 7: (a) Number of adsorbed segments, \(N_{ads}(t)\), versus time \(t\) for regular \(AB\)-copolymers with block size \(M = 1 \div 64\) and length \(N = 256\). For comparison, the transient of a homopolymer is shown by a solid line too. The time interval, taken by the initial "shoulder", is shown in the upper left inset. The lower inset displays the variation of the scaling exponent, \(\alpha\), for the time of adsorption \(\tau \propto N^\alpha\) versus block length relationship. (b) The same as in (a) but for random copolymers of length \(N = 256\) and different composition \(p = 0.25, 0.5, 0.75\). For \(p = 1\) one has the case of a homopolymer. The inset shows the variation of \(\alpha\) with \(p\).

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treated even in such more complicated cases. For random copolymers the role of the block length $M$ would then be played by the typical correlation length.

D. Time evolution of the distribution functions - MC data

One gains most comprehensive information regarding the adsorption process from the time evolution of the different building blocks (trains, loops, and tails) Probability Distribution Functions (PDF) \[30\]. From the MC simulation data, displayed in Fig. 8, for example, one may verify that the resulting distribution $D(h, t)$ of different train lengths is found to be exponential, in close agreement with the theoretically expected shape \[30\], predicted under the assumption that local equilibrium of loops of unit length is established much faster than the characteristic time of adsorption itself. When scaled with the mean train length $h_{av}(t) = \langle h(t) \rangle$, at time $t$, in both cases for $\epsilon/k_BT = 3.0$ and 5.0 one finds an almost perfect straight line in semi-log coordinates. One may thus conclude that $D(h, t)$ preserves its exponential form during the course of the adsorption process, validating thus the conjecture of rapid local equilibrium. The latter however is somewhat violated for the case of very strong adsorption, $\epsilon/k_BT = 5.0$, where the rather scattered data suggests that the process of loop equilibration is slowed down and the aforementioned time separation is deteriorated.

The PDF of loops $W(k, t)$ at different times after the onset of adsorption is shown in Fig. 8. Evidently, the distribution is sharply peaked at size one whereas less than the remaining 20% of the loops are of size two. Thus the loops can be viewed as single thermally activated defects (vacancies) comprising a desorbed single bead with both of its nearest neighbors still attached to the adsorption plane. As the inset in Fig. 8 indicates, the PDF of loops is also described by an exponential function. The PDFs for loops at different time collapse on a master curve, if scaled appropriately with the instantaneous order parameter $n(t)/N$. Eventually, in Fig. 9a we present the observed PDF $T(l, t)$ of tails for different times $t$ after the start of adsorption, and compare the simulation results with those from the numeric solution of Eq. (4.1), taking into account that $T(l, t) = P(N - l, t)$. One may readily verify from Fig. 9 that the similarity between simulational and theoretic results is really strong. In both cases one starts at $t = 1$ with a sharply peaked PDF at the full tail length $l(t = 1) = N$. As time proceeds, the distribution becomes broader and its maximum shifts to smaller values. At late times the moving peak shrinks again and the tail either vanishes, or reduces to a size of single segment which is expressed by the sharp peak at the origin of the abscissa.

Summary

The main focus of this contribution has been aimed at the adsorption transition of random and regular multi-block copolymers on a flat structureless substrate whereby by different means - scaling considerations and computer simulations - a consistent picture of the macromolecule behavior at criticality is derived.
As a central result one should point out the phase diagram of regular multiblock adsorption which gives the increase of the critical adsorption potential $\epsilon_M$ with decreasing length $M$ of the adsorbing blocks. For very large block length, $M^{-1} \to 0$, one finds that the CAP approaches systematically that of a homogeneous polymer.

The phase diagram for random copolymers with quenched disorder which gives the change in the critical adsorption potential, $\epsilon_p^c$, with changing percentage of the sticking $A$-monomers, $p$, is observed to be in perfect agreement with the theoretically predicted result which has been derived by treating the adsorption transition in terms of the “annealed disorder” approximation.

Evidently, a consistent picture of how some basic polymer chain properties of interest such as the gyration radius components perpendicular and parallel to the substrate, or the fraction of adsorbed monomers at criticality, scale when a chain undergoes an adsorption transition emerges regardless of the particular simulation approach. An important conclusion thereby concerns the value of the universal crossover exponent $\phi = 0.5$ which is found to remain unchanged, regardless of whether homo-, regular multiblock-, or random polymers are concerned. Thus the universality class of the adsorption transition of a heteropolymer is the same as that of a homopolymer.

Concerning the adsorption kinetics of a single polymer chain on a flat surface, it is shown that within the “stem-flower” model and the assumption that the segment attachment process follows a “zipping” mechanism, one may adequately describe the time evolution of the adsorbed fraction of monomers and of the probability distribution functions of the various structural building units (trains, loops, tails) during the adsorption process. For regular multiblock and random copolymers it is found that the adsorption kinetics strongly resembles that of homopolymers. The observed deviations from the latter suggest plausible interpretations in terms of polymer dynamics, however, it is clear that additional investigations will be warranted before a complete picture of the adsorption kinetics in this case is established too.

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