# Adsorption of Multiblock and Random Copolymer on a Solid Surface: Critical Behavior and Phase Diagram

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ABSTRACT: The adsorption of a single multiblock AB copolymer on a solid planar substrate is investigated by means of computer simulations and scaling analysis. It is shown that the problem can be mapped onto an effective homopolymer adsorption problem. In particular, we discuss how the critical adsorption energy and the fraction of adsorbed monomers depend on the block length M of sticking monomers A, and on the total length N of the polymer chains. Also the adsorption of the random copolymers is considered and found to be well described within the framework of the annealed approximation. For a better test of our theoretical prediction, two different Monte Carlo (MC) simulation methods were employed: (a) off-lattice dynamic bead-spring model, based on the standard Metropolis algorithm (MA), and (b) coarse-grained lattice model using the pruned-enriched Rosenbluth method (PERM) which enables tests for very long chains. The findings of both methods are fully consistent and in good agreement with theoretical predictions.

#### 1. Introduction

Adsorption of polymers on surfaces plays a key role in numerous technological applications and is also relevant to many biological processes. During the last three decades it has been constantly a focus of research interest. The theoretical studies of the behavior of polymers interacting with solid substrate have been based predominantly on both scaling analysis<sup>1-5</sup> as well as on the self-consistent field (SCF) approach.<sup>7</sup> The close relationship between theory and computer experiments in this field<sup>5,6</sup> has proved especially fruitful. Most investigations focus as a rule on the determination of the critical adsorption point (CAP) location and on the scaling behavior of a variety of quantities below, above, and at the CAP. Thus, an eminent relation between polymer statistics and the corresponding correlation functions<sup>5</sup> in the *n*-vector model of magnets with a free surface in the limit  $n \rightarrow 0$  has led to a number of important results. Special interest has been paid to the determination of the so-called crossover exponent  $\phi$  which is known to govern the fraction of adsorbed monomers at the CAP. Recently, the scaling relationship for a single-chain adsorption has been tested by Monte Carlo (MC) simulation on a cubic lattice<sup>8,9</sup> as well as by an off-lattice model<sup>6,10</sup>,, and the adsorption transition of a polymer could be viewed nowadays as comparatively well understood.

While the investigations mentioned above have been devoted exclusively to homopolymers, the adsorption of copolymers (e.g., multiblocks or random copolymers) is still much less understood. Thus, for instance, the CAP dependence on block size M at fixed concentration of the sticking A-mers is still unknown as are the scaling properties of regular multiblock copolymers in the vicinity of the CAP. From the theoretical perspective, the case of diblock copolymers has been studied mainly within the SCF approach<sup>7,11</sup>. The case of random copolymers adsorption has gained comparatively more attention by researchers so far. It has been investigated by Whittington et al.<sup>12,13</sup> using both the annealed and quenched models of

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randomness. In the latter case, the authors implemented the Morita approximation (which is reduced to an optimization problem with a set of constraints involving the moments of the quenched random probability distribution). The influence of sequence correlations on the adsorption of random copolymers has been studied by means of the variational and replica method approach.<sup>14</sup> Sumithra and Baumgaertner<sup>15</sup> examined the question of how the critical behavior of random copolymers differs from that of homopolymers. Thus, among a number of important conclusions, the results of Monte Carlo simulations demonstrated that the crossover exponent  $\phi$  (see below) is independent of the fraction of attractive monomers *n*.

In the present paper, we use scaling analysis as well as two MC simulation methods to study the critical behavior of multiblock and random copolymers. It turns out that the critical behavior of these two types of copolymers could be reduced to the behavior of an effective homopolymer chain with "renormalized" segments. For the multiblock copolymer this allows, e.g., to explain how the critical attraction energy depends on the block length M and to 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 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 case of annealed randomness. We show that our MC findings close to criticality could be perfectly treated within the annealed randomness model.

# 2. Scaling Properties of Homopolymer Adsorption

**2.1. Order Parameter.** Before discussing copolymers adsorption, we briefly sketch the scaling theory of homopolymer adsorption<sup>5,8,10</sup>. It is well-known that a single polymer chain undergoes a transition from a nonbound into an adsorbed state when the adsorption energy  $\epsilon$  per monomer increases beyond a critical value  $\epsilon_c$ . Here and in what follows  $\epsilon$  is measured in units of the thermal energy  $k_BT$  (with  $k_B$  being the Boltzmann constant and *T* the temperature of the system). The adsorption transition can be interpreted as a second-order phase transition

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at the critical point (CAP) of adsorption  $\epsilon = \epsilon_c$  in the thermodynamical limit, i.e.,  $N \rightarrow \infty$ . 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 5) and  $\phi = 0.484$  (ref 9), we adopt, however, the value  $\phi = 0.50 \pm 0.02$  which has been suggested as the most satisfactory<sup>10</sup> by comparison with comprehensive simulation results.

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  $N \rightarrow \infty$ , the fraction *n* goes to zero  $(\approx \mathcal{O} (1/N))$  for  $\epsilon \ll \epsilon_c$ , then near  $\epsilon_c$ ,  $n \sim N^{\phi-1}$ , and 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 is then

$$n(\eta) = N^{\phi^{-1}} G(\eta) \tag{1}$$

with the scaling function

$$G(\eta) = \begin{cases} \text{const,} & \text{for } \eta \to 0\\ \eta^{(1-\phi)/\phi}, & \text{for } \eta \gg 1 \end{cases}$$
(2)

The resulting scaling behavior of n follows as

$$n \propto \begin{cases} 1/N, & \text{for } \kappa \ll 0\\ N^{\phi-1}, & \text{for } \kappa \to 0\\ \kappa^{(1-\phi)/\phi}, & \text{for } \kappa \gg 1 \end{cases}$$
(3)

**2.2. Gyration Radius.** The gyration radius in direction perpendicular to the surface,  $R_{g\perp}(\eta)$ , has the form

$$R_{g\perp}(\eta) = a N^{\nu} \mathcal{G}_{g\perp}(\eta) \tag{4}$$

One may determine the form of the scaling function  $\mathcal{G}_{g\perp}(\eta)$  from the following consideration. At  $\kappa < 0$  one has  $R_{g\perp} \sim aN^{\nu}$ , so that  $\mathcal{G}_{g\perp} = \text{const.}$  In the opposite limit  $\eta \gg 0$  the  $N - \mathcal{G}_{g\perp}(\eta \sim \eta^{-\nu/\phi})$ . Thus

$$\mathcal{G}_{g\perp}(\eta) = \begin{cases} \text{const, for } \eta \le 0\\ \eta^{-\nu/\phi}, \text{ for } \eta \gg 0 \end{cases}$$
(5)

As a result

$$R_{g\perp}(\eta) \propto \begin{cases} a N^{\nu}, & \text{for } \eta \le 0\\ \kappa^{-\nu/\phi}, & \text{for } \eta \gg 0 \end{cases}$$
(6)

The gyration radius in direction parallel to the surface has similar scaling representation:

$$R_{\rm g||}(\eta) = a N^{\nu} \mathcal{G}_{\rm g||}(\eta) \tag{7}$$

Again at  $\kappa < 0$  the gyration radius  $R_{gll} \sim aN^{\nu}$  and  $\mathcal{G}_{gll} = \text{const.}$ At  $\eta \gg 0$  the chain behaves as a two-dimensional self-avoiding walk (SAW), i.e.,  $R_{gll} \sim aN^{\nu_2}$ , where  $\nu_2 = 3/4$  denotes the Flory exponent in two dimensions. In result, the scaling function behaves as

$$\mathcal{G}_{g|l}(\eta) = \begin{cases} \text{const,} & \text{at } \eta \le 0\\ \eta^{(\nu_2 - \nu)/\phi}, & \text{at } \eta \gg 0 \end{cases}$$
(8)

Thus

$$R_{g|l}(\eta) \propto \begin{cases} aN^{\nu}, & \text{at } \eta \le 0\\ \kappa^{(\nu_2 - \nu)/\phi} N^{\nu_2}, & \text{at } \eta \gg 0 \end{cases}$$
(9)

2.2.1. Blob Picture. 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  $k_{\rm B}T$  each. The thickness of the pancake  $R_{g\perp}$  corresponds to the size of the blob and the chain conformation within a blob stays unperturbed (i.e., it is simply a SAW), thus  $g \sim (R_{g\perp}/a)^{1/\nu} = \kappa^{-1/\phi}$  where we have used eq 6. The gyration radius can be represented thus as

$$R_{\rm gll} = R_{\rm gl} \left(\frac{N}{g}\right)^{\nu_2} \propto \kappa^{(\nu_2 - \nu)/\phi} N^{\nu_2} \tag{10}$$

and one goes back to eq 9 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. For example, we could recast the order parameter scaling behavior eq 1 as

$$n = N^{\phi^{-1}} H\!\left(\frac{N}{g}\right) \tag{11}$$

where H(x) denotes a new scaling function:

$$H(x) = \begin{cases} \text{const, for } x \to 0\\ x^{1-\phi}, \text{ for } x \gg 1 \end{cases}$$
(12)

2.2.2. Ratio of Gyration Radius Components. 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  $\epsilon_c$  (see refs 8 and 10). In fact, from the previous scaling equations

$$r(\eta) = \frac{R_{g\perp}(\eta)}{R_{g|}(\eta)} = \frac{\mathcal{G}_{g\perp}(\eta)}{\mathcal{G}_{g|}(\eta)}$$
(13)

Hence at the critical point, i.e., at  $\eta \rightarrow 0$ , the ratio r(0) = 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  $\epsilon_c$ .

Another way to fix  $\epsilon_c$  is the following. Exactly at the critical point  $n \sim N^{\phi-1}$ , so that by plotting  $nN^{1-\phi}$  vs N at different values of  $\epsilon$  one can determine the value  $\epsilon \approx \epsilon_c$  under which  $nN^{1-\phi}$  becomes independent of N.

**2.3. Free Energy of Adsorption.** The adsorption on a surface at  $\kappa > 0$  is due to a free energy gain which is proportional to the number of blobs, i.e.

$$\frac{F - F_{\text{bulk}}}{N} \propto -\frac{1}{g} \sim -\kappa^{1/\phi} \tag{14}$$

The expression for the specific heat per monomer follows immediately from eq 14 as

$$C_{\rm V} = -\frac{\partial^2 (F - F_{\rm bulk})}{\partial^2 \kappa} \propto \kappa^{-\alpha} \tag{15}$$

where  $\alpha = 2 - \phi^{-1}$ . Note that a factor of  $k_{\rm B}T$  is absorbed in the free energy throughout the paper. If  $\phi = 0.5$  then  $\alpha = 0$  and the specific heat undergoes a jump at the CAP (cf. section 6.1.2).

For a chain (of the length *N*) on the verge of adsorption, the foregoing free energy gain,  $F - F_{\text{bulk}}$ , should be of the order of unity. In view of eq 14, this gives an estimate for the critical energy of adsorption, CAP

$$\epsilon_{\rm c}(N) = \epsilon_{\rm c}(\infty) \left( 1 + \frac{1}{N^{\phi}} \right) \tag{16}$$

where we have explicitly marked the CAP,  $\epsilon_c(N)$  and  $\epsilon_c(\infty)$ , for finite and infinitely long chains, respectively.

#### 3. Multiblock Copolymer Adsorption

Consider now the adsorption of a regular multiblock copolymer which is built up from 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 multiblock AB copolymer, we reduce the problem to that of a homopolymer **2922** Bhattacharya et al.

which has been considered above. The idea is that a regular multiblock copolymer can be considered as a "homopolymer" where a single AB diblock plays the role of an effective monomer.<sup>18</sup> For such a mapping we first estimate the effective energy of adsorption per diblock.

**3.1. Effective Energy of Adsorption Per Diblock.** Each individual diblock is made up of an attractive A block of length M and a neutral B block of the same length M. Upon adsorption, the attractive A block forms a string of blobs whereas the B part forms a nonadsorbed tail (or loop) (see Figure 1).

The free energy gain of the attractive block may be written according to eq 14 as

$$F_{\rm attr} = -\kappa^{1/\phi} M \tag{17}$$

where we measure the energy in units of  $k_{\rm B}T$  and  $\kappa \equiv (\epsilon - \epsilon_{\rm c}^{\rm h})/\epsilon_{\rm c}^{\rm h}$  measures the normalized distance from the CAP  $\epsilon_{\rm c}^{\rm h}$  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

$$F_{\rm rep} = (\gamma - \gamma_{11}) \ln M \tag{18}$$

where the universal exponents  $\gamma$  and  $\gamma_{11}$  are well-known<sup>17</sup> (e.g., in 3D space  $\gamma = 1.159$ ,  $\gamma_{11} = -0.390$ ). In the case that also the tails are involved, one should also use the exponent  $\gamma_1 =$ 0.679 albeit this does not change qualitatively the expression eq 18. They enter the partition function expressions for a free chain, a chain with both ends fixed at a two points, and for a chain, tethered by the one end.<sup>17</sup> In result the effective adsorption energy of a diblock is

$$E(M) = \kappa^{1/\phi} M - (\gamma - \gamma_{11}) \ln M \tag{19}$$

One may see from Figure 1b that the number of A monomers in the immediate vicinity of the attractive wall substantially exceeds (by a factor of 30) the number of B monomers, although the chain is at the critical threshold for adsorption. The theoretical treatment which follows below takes this into account.

**3.2. Order Parameter.** Now we consider a "homopolymer" which is build up from effective units (diblocks), with the attractive energy given by eq 19. Let us denote the total number of such effective units by  $\mathcal{N} = N/2M$ . The fraction of effective units on the surface obeys then the same scaling law as given by eq 1, i.e.

$$\frac{\mathcal{N}_{s}}{\mathcal{N}} = \mathcal{N}^{\phi-1} G(\Delta \mathcal{N}^{\phi})$$
(20)

where now  $\Delta \equiv (E - E_c^h)/E_c^h$  with the critical adsoption energy  $E_c^h$  of the renormalized homopolymer. Generally, one would expect  $E_c^h$  to be of the order of  $\epsilon_c^h$  albeit for different models both critical energies would probably differ from each other. Equation 20 is accurate if one requires that (i)  $\kappa \ll 1$  but  $M \gg 1$  such that  $\ln M \gg 1$  and  $\kappa^{1/\phi}M \gg 1$ , and (ii)  $\mathcal{N} \gg 1$ . The effective attraction *E* of a segment of the renormalized chain now depends on *M* according to eq 19.

Within each effective unit only  $M_s$  A monomers will be adsorbed at criticality whereby this monomer number scales as

$$M_{\rm s} = M^{\phi} G(\kappa M^{\phi}) \tag{21}$$

with  $\kappa \equiv (\epsilon - \epsilon_c^{\rm h})/\epsilon_c^{\rm h}$ .

The total number of adsorbed monomer is given by

$$N_{\rm s} = \mathcal{N}_{\rm s} M_{\rm s} = \mathcal{N}_{\rm s} M^{\phi} G \left( \kappa M^{\phi} \right) \tag{22}$$

It follows that the fraction

$$n \equiv \frac{N_s}{N} = \frac{\mathcal{N}_s}{N} M^{\phi} G(\kappa M^{\phi})$$
$$= \frac{\mathcal{N}_s}{2N} M^{\phi^{-1}} G(\kappa M^{\phi})$$
$$= \frac{1}{2} M^{\phi^{-1}} G(\kappa M^{\phi}) \left(\frac{N}{2M}\right)^{\phi^{-1}} G\left(\Delta \left(\frac{N}{M}\right)^{\phi}\right)$$
(23)

where we have used the scaling law, eq 20, for the effective units. Hence, the final expression for the order parameter can be written as follows:

$$n = \frac{1}{2^{\phi}} N^{\phi-1} G(\kappa M^{\phi}) G\left(\Delta \left(\frac{N}{M}\right)^{\phi}\right)$$
(24)

Thus we have expressed the order parameter *n* of a multiblock copolymer in terms of the chain length *N*, the block length *M*, and the monomer attraction energy  $\epsilon$  as well as the model-dependent homopolymer critical attraction energy  $E_c^{h}$ . Let us consider now some limiting cases.

3.2.1. Close to Criticality  $\Delta = 0$ . 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



**Figure 1.** (a) Schematic representation of an individual adsorbed AB diblock. The A part forms a string of quasi-two-dimensional blobs and the B part is neutral regarding the substrate and its contribution to the free energy is of pure entropical nature. (b) Density profiles against distance *z* from the adsorbing plane of A and B monomers at the CAP  $\epsilon_{ads} = 2.12$  for a chain with N = 256 and block size M = 8. In the inset this is magnified for better visibility. The ratio of the number of A and B monomers in the immediate vicinity of the attractive wall is about 30.

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where we have used eq 19 and set  $\phi = 0.5$ . Under this condition, the second G function in eq 24 is a constant, i.e., G(0) = const.On the other hand, with respect to a single effective unit the chain stays far from the criticality because of

$$\kappa_{\rm c}^{\rm M} \sqrt{M} = \sqrt{(\gamma - \gamma_{11}) \ln M + E_{\rm c}^{\rm h}} \gg 1$$
 (26)

Equation 26 reflects our simulation result, cf. Figure 1b, and justifies the consideration of A monomers as a string of blobs. In this case the first *G* function in eq 24 behaves as  $G(\kappa_c^M \sqrt{M}) \sim \kappa_c^M \sqrt{M}$ , where  $\kappa_c^M$  now is fixed by eq 25. As a result, eq 24 becomes

$$n \propto \left(\frac{(\gamma - \gamma_{11})\ln M + E_{\rm c}^{\rm h}}{N}\right)^{1/2} \tag{27}$$

3.2.2. State of the Strong Adsorption. In this regime  $\kappa \sqrt{M} \gg 1$  and  $\Delta \sqrt{N/M} \gg 1$  so that  $n \simeq (1/\sqrt{N})G(\kappa \sqrt{M})G(\Delta \sqrt{N/M}) \sim \kappa \Delta$ . Therefore

$$n \simeq \frac{\kappa [\kappa^2 M - (\gamma - \gamma_{11}) \ln M - E_{\rm c}^{\rm h}]}{E_{\rm c}^{\rm h}}$$
(28)

**3.3. Gyration Radius.** The components of the gyration radius of a multiblock copolymer can be treated again by making use of the mapping on the homopolymer problem given by eqs 4 and 7. In doing so the mapping looks as follows:

$$a \to aM^{\nu}$$

$$\kappa \to \Delta = \frac{E - E_{\rm c}^{\rm h}}{E_{\rm c}^{\rm h}}$$

$$N \to \mathcal{N} = \frac{N}{2M}$$
(29)

Thus the gyration radius component in direction perpendicular to the surface becomes

$$\mathscr{R}_{g\perp} = aN^{\nu}\mathscr{G}_{g\perp} \left(\Delta \left(\frac{N}{M}\right)^{\phi}\right) \tag{30}$$

In the strong adsorption limit  $\Delta \sqrt{N/M} \gg 1$  and  $\Re_{\perp} \sim a \Delta^{-\nu/\phi} M^{\nu}$ , which yields

$$\mathcal{R}_{\perp} \simeq \frac{aM^{\nu}E_{c}^{h2\nu}}{[\kappa^{2}M - (\gamma - \gamma_{11})\ln M - E_{c}^{h}]^{2\nu}}$$
(31)

In a similar manner, the gyration radius component parallel to the surface has the form

$$\mathcal{R}_{\text{gll}} = aN^{\nu}\mathcal{G}_{\text{gll}}\left(\Delta\left(\frac{N}{M}\right)^{\phi}\right) \tag{32}$$

which in the limit  $\Delta \sqrt{N/M} \gg 1$  results in

$$\mathcal{R}_{g|l} \simeq a \left( \frac{\Delta^{1/\phi}}{M} \right)^{\nu_2 - \nu} N^{\nu_2} \\ \simeq \frac{a [\kappa^2 M - (\gamma - \gamma_{11}) \ln M - E_c^h]^{2(\nu_2 - \nu)}}{M^{\nu_2 - \nu}} N^{\nu_2}$$
(33)

Like in the homopolymer case, one can define a blob length  $g_{\rm eff} \sim (\mathscr{R}_{\perp}/a)^{1/\nu} \sim \Delta^{-1/\phi}M$  which in the strong adsorption limit,  $\Delta \geq 1$ , approaches the block length,  $g_{\rm eff} \simeq M$ , as it should be. Also in the limit of strong adsorption,  $\Delta \sqrt{N/M} \gg 1$ , the ratio

$$\frac{\mathscr{R}_{\text{gll}}}{\mathscr{R}_{\perp}} \simeq \left(\frac{\Delta^{1/\phi} N}{M}\right)^{\nu_2} \simeq \left(\frac{N}{g_{\text{eff}}}\right)^{\nu_2} \tag{34}$$

leads to the correct scaling in terms of number of blobs.

#### 4. Random Copolymer Adsorption

Consider a random copolymer which is built up of  $N_p$  A-type and  $N_h$  B-type monomers. The sampled AB sequences are frozen (i.e., a distinct sample does not change during the measurement) which corresponds to quenched disorder. The binary variable  $\sigma$  specifies the arrangement of monomers along the chain, so that  $\sigma = 1$ , if the monomer is of A-type (A monomers attract to the surface) and  $\sigma = 1$  otherwise (i.e., in case of neutral B monomers). Let the fraction of attractive monomers (i.e., the composition) be  $p = N_p/N$  and the fraction of neutral ones be  $1 - p = N_h/N$  We assume that the statistics of sequences is governed by the Bernoulli distribution,<sup>20</sup> i.e., the corresponding distribution function looks like

$$P\{\sigma\} = p\delta(1-\sigma) + (1-p)\delta(\sigma) \tag{35}$$

This distribution is a special case of the more general Markovian copolymers<sup>20</sup> when the "chemical correlation length" goes to zero. Two statistical moments which correspond to the distribution eq 35 are

$$\langle \sigma \rangle = p$$

$$\langle \theta^2 \rangle \equiv \langle [\sigma - \langle \sigma \rangle]^2 \rangle = p(1-p)$$
(36)

**4.1. How Does the Critical**  $\epsilon_c$  **Depend on the Composition** p? The adsorption of a random copolymer on a homogeneous surface has been studied by Whittington et al.<sup>12,13</sup> 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, as a matter of fact, one samples all possible distributions of monomers sequences along the backbone of the macromolecule. Following this assumption,<sup>12</sup> 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.

$$Z(\epsilon) = \sum_{n=1}^{N} \sum_{n_{p}=0}^{n} c_{N}^{+}(n) {\binom{n}{n_{p}}} p^{n_{p}} (1-p)^{n-n_{p}} e^{\epsilon n_{p}}$$

$$= \sum_{n=1}^{N} c_{N}^{+}(n) [p e^{\epsilon} + 1 - p]^{n} = \sum_{n=1}^{N} c_{N}^{+}(n) e^{n\epsilon_{eff}^{h}}$$
(37)

where  $\epsilon_{\text{eff}}^{\text{h}}$  is the attraction energy of an effective homopolymer. From eq 37 one can see that the annealed problem is reduced to that of a homopolymer where the effective attractive energy is defined as

$$\epsilon_{\rm eff}^{\rm h} = \ln[p \mathrm{e}^{\epsilon} + 1 - p] \tag{38}$$

We know that at the critical point the homopolymer attraction energy,  $\epsilon_{\text{eff}}^{\text{h}} = \epsilon_{\text{c}}^{\text{h}}$ , is model dependent. Then the critical attraction energy  $\epsilon = \epsilon_{\text{R}}^{\text{p}}$  of a random copolymer reads

$$\epsilon_{\rm c}^{\rm p} = \ln \left[ \frac{\exp \epsilon_{\rm c}^{\rm h} + p - 1}{p} \right] \ge \epsilon_{\rm c}^{\rm h} \tag{39}$$

where the composition  $0 \le p \le 1$ . At  $p \to 0$ ,  $\epsilon_{\mathbb{R}}^p \to \infty$  whereas at p = 1,  $\epsilon_{\mathbb{R}}^p = \epsilon_{\mathbb{R}}^b$ . The relationship in eq 39 has been recently found to be confirmed by Monte Carlo simulations.<sup>19</sup>

#### 5. Simulation Methods

To check the theoretical predictions mentioned in the previous sections, we performed Monte Carlo simulations and investigated the adsorption of a homopolymer, multiblock copolymers, and random copolymers on flat surfaces. Two coarse-grained models, the bead spring model and the simple cubic lattice model, Figure 2, are used, and two different Monte Carlo algorithms, the Metropolis algorithm (MA) and pruned-enriched Rosenbluth method (PERM), are applied to the two models, respectively.

**5.1. Off-Lattice Bead Spring Model with MA.** We have used a coarse grained off-lattice bead spring model<sup>6</sup> to describe

the polymer chains. Our system consists of a single chain tethered at one end to a flat structureless surface. 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 square well potential  $U_w(z) = \epsilon$  (for  $z < \delta$  and  $U_w(z) = 0$  otherwise. Here  $\epsilon/k_BT$  is varied from 0.6 to 3.6. The effective bonded interaction is described by the FENE (finitely extensible nonlinear elastic) potential.

$$U_{\text{FENE}} = -K(1 - l_0)^2 \ln \left[ 1 - \left( \frac{l - l_0}{l_{\text{max}} - l_0} \right)^2 \right]$$
(40)

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

$$\frac{U_{\rm M}(r)}{\varepsilon_{\rm M}} = \exp(-2\alpha(r-r_{\rm min})) - 2\exp(-\alpha(r-r_{\rm min})) \quad (41)$$

with  $\alpha = 24$ ,  $r_{\min} = 0.8$ ,  $\epsilon_M / k_B T = 1$ .

We use periodic boundary conditions in the x-y directions and impenetrable walls in the z direction. We have studied polymer chains of lengths 32, 64, 128, 256, and 512. We have also studied homopolymer chains and random copolymers (with a fraction of attractive monomers, p = 0.25, 0.5, 0.75). The size of the box was  $64 \times 64 \times 64$  in all cases except for the 512 chains where we used a larger box size of  $128 \times 128 \times$ 128. The standard Metropolis algorithm was employed to govern the moves with self-avoidance automatically incorporated in the potentials. In each Monte Carlo update, a monomer was 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 was calculated from the change  $\Delta U$  of the potential energies before and after the move as  $W = \exp(-\Delta U/k_{\rm B}T)$ . As for standard Metropolis algorithm, the attempted move was accepted if Wexceeds a random number uniformly distributed in the interval [0,1]. As a rule, the polymer chains were originally equilibrated in the MC method for a period of about 10<sup>6</sup> MCS (depending on the degree of adsorption  $\epsilon$  and chain length N, this period is varied) whereupon one performs 200 measurement runs, each of length 8  $\times$  10<sup>6</sup> 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.

**5.2.** Coarse-Grained Lattice Model with PERM. The adsorption of AB block copolymer with one end (monomer A) grafted to a plane impenetrable surface and with only monomers A attractive to the surface are described by SAWs of N - 1 steps on a simple cubic lattice with restriction  $z \ge 0$ . There is

an attractive interaction between monomers A and the wall. The partition sum now is written as

$$Z_{N}^{(1)}(q) = \sum_{N_{s}} A_{N}(N_{s})q^{N_{s}}$$
(42)

where  $A_N(N_s)$  is the number of configurations of SAWs with N steps having  $N_s$  sites on the wall, and  $q = e^{\epsilon/k_B}T$  ( $k_BT = 1$ ) hereafter) is the Boltzmann factor,  $\epsilon > 0$  is the attractive energy between the monomer A and the wall. As  $q \rightarrow 1$ , there is no attraction between the monomer A and the wall. On the other hand, it becomes clear that any copolymer will collapse onto the wall, if q becomes sufficiently large. Therefore, we expect a phase transition from a grafted but otherwise detached to an adsorbed phase, similar to the transition observed also for homopolymers.

For our simulations, we use the pruned-enriched Rosenbluth method (PERM)<sup>21</sup> which 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, 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,  $w_i \rightarrow w_i/p_i$ , where  $p_i$  is the probability for putting the monomer at step t. 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  $Z_n = (1/M_n) \Sigma_{\text{config}} W_n$  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 method, we simulate homopolymers of length N = 2048 and multiblock copolymers with block size  $M = 2^k k = 0, 1, 2, \dots, 9$ , The number of monomers is increased to N = 8192 as the block size increases. There are  $10^{5}/10^{6}$  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.

#### 6. Simulation Results

**6.1. Determination of the Critical Point of Adsorption.** The determination of the critical adsorption point (CAP) is essential for testing the scaling results and for comparison with theory. In this work, we determine the CAP from the analysis of several quantities: the order parameter n, the variance of the



Figure 2. Schematic representation of a grafted chain close to criticality. (a) Snapshot of a chain with length N = 128 from the MA model and block size M = 2; (b) N = 2048 with M = 8 from the PERM simulation.



**Figure 3.** Order parameter *n* against the adsorption energy  $\epsilon$  for homopolymers of different chain lengths *N*. The value of the CAP  $\epsilon_c^h(N)$  for  $N \rightarrow \infty$  is extrapolated from the log–log plot of  $\epsilon_c^h(N)$  versus 1/N as shown in the inset. In the thermodynamic limit (a)  $\epsilon_c^h \approx 1.716$  (MA off-lattice model), (b)  $\epsilon_c^h \approx 0.284$  (PERM on a cubic lattice).



Figure 4. Order parameter *n* plotted as a function of attractive energy  $\epsilon$  for copolymers with block size M = 2. The extrapolation plots for  $\epsilon_c(N)$  versus 1/N for block sizes M = 1, 2, 4, 8, 16, and for the homopolymer, plotted versus 1/N, are shown in the inset. (a) MA model, (b) PERM.

number of adsorbed monomers,  $C_v$ , and the gyration radius  $R_g$ . These methods are described as follows:

6.1.1. CAP from the Order Parameter. From the plots of the order parameter n against the adsorption energy  $\epsilon$  for chains of different length N we determine the CAP as the point where the tangent taken at the inflection point of the order parameter curve intersects the horizontal axis  $\epsilon$ . The results are shown in Figure 3 for homopolymers and in Figure 4 for multiblock copolymer with block size M = 2. In Figures 3a and 4a the data is obtained by MA method in our off-lattice model, while in Figures 3b and 4b the data is obtained by PERM for selfavoiding chains on a cubic lattice. Evidently, in both cases the order parameter n increases with growing strength of the substrate potential  $\epsilon$ . Thus, the polymer chain undergoes a transition from a grafted, but otherwise detached state, to an adsorbed state whereby the chain lies flat on the surface plane, see Figure 2b. The transition region narrows down as Nincreases, which is in good agreement with the scaling prediction of n, eq 16, in all cases. In the inset of Figures 3 and Figure 4, we see that the critical point  $\epsilon_{\rm c}^{\rm h}(N)$  for homopolymers of chain length N as well as the critical points  $\epsilon_{\rm c}^{\rm M}(N)$  for multiblock copolymers of chain length N with M = 1, M = 2, M = 4, M= 8, and M = 16, gradually increase as  $N \rightarrow \infty$ . By extrapolating the data to 1/N = 0, one obtains the CAP values in the thermodynamic limit. Results for  $\epsilon_c^h$ , obtained from the analysis of the order parameter, MA and PERM, are listed in Tables 1 and 2. In the last column of both tables we give the estimate from the intersection point of the respective  $R_g$  data. We should point out here that the simulation with the MA model requires

considerable computational effort for  $N \ge 512$ ; therefore, with the PERM method we confine ourselves to chain lengths not large than N = 2048 (Figure 3b), which are considerably shorter than feasible.<sup>9</sup> Nevertheless, our estimate of the CAP  $\epsilon_c^h =$ 0.285(3) is in good agreement with previous results<sup>9</sup> (within the error bars) although corrections to scaling have not been considered here.

6.1.2. From the Variance of the Order Parameter. In a computer simulation, one usually computes the variance of the order parameter,  $\Delta f$ , which yields some important thermodynamic quantities like isothermal compressibility, and/or specific heat, via the fluctuation relations.

$$N^{2}\Delta n = \langle N_{s}^{2} \rangle - \langle N_{s} \rangle^{2}$$

$$\tag{43}$$

At the CAP  $\Delta_n$  has a maximum which becomes larger and narrower as one approaches the thermodynamic limit,  $N \rightarrow \infty$ .

| Table 1. MA |         |          |           |           |             |             |  |  |  |  |  |
|-------------|---------|----------|-----------|-----------|-------------|-------------|--|--|--|--|--|
| M/N         | 64      | 128      | 256       | 512       | $^{\infty}$ | $R_{\rm g}$ |  |  |  |  |  |
| 1           | 2.47(3) | 2.58(3)  | 2.63(3)   | 2.63(3)   | 2.672(30)   | 2.65(3)     |  |  |  |  |  |
| 2           | 2.32(3) | 2.44(3)  | 2.47(3)   | 2.48(3)   | 2.52(2)     | 2.52(3)     |  |  |  |  |  |
| 4           | 2.13(3) | 2.260(3) | 2.29(3)   | 2.29(3)   | 2.34(2)     | 2.30(4)     |  |  |  |  |  |
| 8           | 1.93(3) | 2.08(3)  | 2.12(3)   | 2.14(3)   | 2.19(3)     | 2.06(4)     |  |  |  |  |  |
| 16          | 1.76(3) | 1.93(3)  | 2.00(3)   | 2.01(3)   | 2.06(3)     | 1.95(4)     |  |  |  |  |  |
| p/N         |         |          |           |           |             |             |  |  |  |  |  |
| 1.0         | 1.62(2) | 1.66(2)  | 1.701(20) | 1.698(25) | 1.716(20)   | 1.718(20)   |  |  |  |  |  |
| 0.75        | 1.83(2) | 1.89(2)  | 1.92(2)   | 1.946(20) | 1.95(3)     | 1.95(3)     |  |  |  |  |  |
| 0.50        | 2.21(2) | 2.25(2)  | 2.29(2)   | 2.32(2)   | 2.33(2)     | 2.38(5)     |  |  |  |  |  |
| 0.25        | 2.81(4) | 2.97(4)  | 2.98(4)   | 3.02(4)   | 3.05(5)     | 2.91(6)     |  |  |  |  |  |

 $N\Delta n$ 

| M/N    | 64        | 128       | 256      | 512      | 1024     | ~        | $R_{ m g}$ |  |  |  |
|--------|-----------|-----------|----------|----------|----------|----------|------------|--|--|--|
| 1      | 0.337(9)  | 0.457(5)  | 0.505(5) | 0.535(3) | 0.548(2) | 0.560(2) | 0.568(6)   |  |  |  |
| 2      | 0.322(4)  | 0.438(4)  | 0.486(3) | 0.516(2) | 0.536(2) | 0.545(8) | 0.556(3)   |  |  |  |
| 4      | 0.296(7)  | 0.411(4)  | 0.465(3) | 0.489(3) | 0.511(2) | 0.520(4) | 0.524(2)   |  |  |  |
| 8      | 0.368(4)  | 0.422(4)  | 0.455(2) | 0.464(3) | 0.474(2) | 0.480(2) | 0.478(3)   |  |  |  |
| 16     | 0.320(4)  | 0.385(4)  | 0.411(2) | 0.426(3) | 0.432(2) | 0.441(2) | 0.437(4)   |  |  |  |
| p/N    |           |           |          |          |          |          |            |  |  |  |
| 1.0    | 0.173(4)  | 0.223(4)  | 0.250(3) | 0.267(4) | 0.278(2) | 0.285(3) | 0.286(3)   |  |  |  |
| 0.75   | 0.241(10) | 0.294(6)  | 0.325(5) | 0.346(3) | 0.352(3) | 0.363(2) | 0.366(2)   |  |  |  |
| 0.50   | 0.370(20) | 0.439(15) | 0.469(8) | 0.485(5) | 0.499(4) | 0.507(2) | 0.509(2)   |  |  |  |
| 0.25   | 0.77(2)   | 0.78(2)   | 0.82(1)  | 0.83(2)  | 0.83(2)  | 0.843(6) | 0.845(4)   |  |  |  |
| 0.25/N | 100       | 200       | 400      | 800      | 1600     |          |            |  |  |  |
|        |           |           |          |          |          |          |            |  |  |  |

In Figure 5a this is shown for the PERM model along with an extrapolation of the CAP  $\epsilon_c^h(N)$  for chains of length N (see inset) which for  $N \rightarrow \infty$  becomes a straight line in agreement with eq 16. It becomes also evident from Figure 5b that the alternative method of using the position of the maximum of the specific heat,  $C_{\rm V} = (k_{\rm B} \tilde{T}^2)^{-1} (\langle U^2 \rangle - \langle U \rangle^2)$  from the fluctuations of the internal energy,  $U = \epsilon N_s$ , does not give satisfactory results due to the rather flat shape of the maximum. This behavior is not surprising, if one recalls that the critical exponent  $\alpha$  describing the divergence of  $C_V$  at the CAP, i.e., for  $\kappa \rightarrow 0$ , according to  $C_{\rm V} \propto \kappa^{-\alpha}$  (see eq 15) is given by  $\alpha = 2 - \phi^{-1} \approx 0.^{22}$  It has been shown earlier,<sup>22</sup> however, that one can still use specific heat data to determine the CAP if, instead of the position of the maximum, one examines the common intersection point of  $C_{\rm V}$  vs  $\epsilon$ . In our simulation this yields again  $\epsilon_c^h = 0.284$  (cf. Table 2).

6.1.3. From the Components of  $R_g$ . According to eqs 6, 9, and 13, one should expect that all curves of  $R_{g\perp}^2/R_{g|l}^2$ , for different chain length N intersect at a fixed point which gives

the CAP in the limit of  $N \rightarrow \infty$ . In Figure 6, we illustrate this method by plotting the ratio  $R_{g\perp}^2/R_{g\parallel}^2$  vs  $\epsilon$  for copolymers with block size M = 2. For both methods, MA and PERM, the curves for different *N* intersect nearly at a single intersection point; however, as before, the CAP determined by MA (see Figure 6a) is less accurate than the results given by PERM (see Figure 6b). The CAPs obtained from this method,  $\epsilon_c^{M=2} = 2.52(3)$  by MA and  $\epsilon_c^{M=2} = 0.556(4)$  by PERM are consistent with the estimates from the order parameter method where  $\epsilon_c^{M=2} = 2.521(20)$  by MA and  $\epsilon_c^{M=2} = 0.546(8)$  by PERM. The CAPs  $\epsilon_c^M$  for homopolymers, multiblock copolymers with different block size *M*, and for random copolymers are listed in Tables 1 and 2.

**6.2. Scaling Behavior.** From the data for the CAP one may check the value of the crossover exponent  $\phi = 0.50$  by plotting the order parameter *n* vs *N* (eq 3). This is illustrated in Figure 7 as a double logarithmic plot of *n* vs *N* for the case of M = 1, i.e., regular alternating polymers. Figure 7 demonstrates clearly



**Figure 5.** Results for (a) the variance of the order parameter *n* multiplied by *N* in the case of a homopolymer. The inset shows an extrapolation of the CAP  $\epsilon_c^h(N)$  for  $1/N^{\phi} \rightarrow 0$  which converges to the value for an infinite chain,  $\epsilon_c^h = 0.284$  (cf. Table 2). (b) Specific heat per monomer,  $C_V/N$ , which is plotted as a function of  $\epsilon$  for homopolymers of different chain length N.<sup>21</sup>



Figure 6. Ratio of  $R_{g\perp}^2/R_{g\parallel}^2$  plotted as a function of  $\epsilon$  for copolymers with block size M = 2. The critical point is determined by the intersection of all curves which are found to be at (a)  $\epsilon_c^{M=2} \approx 2.52$  (MA) and (b)  $\epsilon_c^{M=2} \approx 0.556$  (PERM).



Figure 7. log-log plot of the order parameter *n* vs *N* for block copolymers with block size (M = 1). The value of  $\epsilon$  for each curve is given in the legend while the slope is also indicated. One may readily check that the straight lines with slope 0.5 correspond to the respective values of  $\epsilon_c$  in both models, (a) MA and (b) PERM.



**Figure 8.** log-log plots of the scaled order parameter  $nN^{1-\phi}$  and the gyration radius components  $R_{gl}^2/N^{2\nu}$  and  $R_{g.}^2/N^{2\nu}$  vs  $kN^{\phi}$  with  $\nu = 0.588$  and  $\nu_2 = 3/4$ . The straight lines indicate the asymptotic behaviour of the scaling functions given by eqs 24, 6, and 9: (a) and (b) represent results for regular multiblock copolymers with block size M = 8 and are obtained by MA; (c) and (d) similar results but for M = 16 are obtained by PERM.

that the slope of the *n* vs *N* curves in logarithmic coordinates is equal to  $\phi - 1 = -0.5$  only in those cases where the strength of the substrate potential equals the CAP value  $\epsilon_c$ , in agreement with the relation  $n \propto N^{\phi-1}$ . As in the case of homopolymers (eq 3), Figure 7a shows that in the strongly adsorbed regime ( $\epsilon$ = 3.40) above the CAP the order parameter  $n \propto N^0$  (*all* monomers stick). In contrast, far below the CAP, only the anchoring monomer is attached to the substrate,  $n \sim N^{-1}$ , as in the asymptotic limit  $N \rightarrow \infty$  of homopolymers. This is observed for  $\epsilon = 0.60$  for the alternating chains (M = 1). In Figure 7b, where the statistical precision and the chain lengths involved are much higher, one may see that for large *N* the curves which are slightly above,  $\epsilon = 0.571$ , or below,  $\epsilon = 0.560$ , the CAP at  $\epsilon = 0.568$  (cf. Figure 6) display slopes which differ slightly from -0.5 and thus considerably narrow the interval of critical behavor.

In Figure 8 we present the results for the components of the mean square gyration radius,  $R_{gll}^2$  and  $R_{g\perp}^2$ , in scaled form in terms of the parameter  $kN^{\phi}$  for regular block copolymers with block size M = 1 and M = 8. Generally, one observes a good



Figure 9.  $k_c^{\rm m} = (\epsilon_c^{\rm m} - \epsilon_c^{\rm m})/\epsilon_c^{\rm h}$  plotted vs 1/*M* for multiblock copolymers with various values of *M*. The critical points of adsorption for homopolymers are (a)  $\epsilon_c^{\rm h} = 1.716$  (MA) and (b)  $\epsilon_c^{\rm h} = 0.285$  (PERM). The curves give the best fit of eq 25,  $k \propto ((\gamma - \gamma_{11}) \ln(M) + E_c^{\rm h})/M)^{1/2}$ . Note that the block size  $1 \le M \le 16$  in (a), and  $1 \le M \le 512$  in (b).



Figure 10. Same as in Figure 7 but for random copolymers with the composition p = 0.5 (a) MA where  $\epsilon g = 2.33$  and (b) PERM with  $\epsilon g = 0.507$ .

agreement with the predictions of section 2, especially concerning the data obtained by PERM, Figure 8c,d. Considerable deviations from the expected scaling behavior are observed only in Figure 8b where the effective segment of a diblock with M= 8 is comparatively large for the simulated chain lengths  $N \le$ 512, meaning effective chain lengths of  $N_{\rm eff} = N/16 \le 32$  which are definitely too short for a well-pronounced scaling behavior to be demonstrated. With the much longer chains,  $N \le 2048$ , sampled by PERM and shown in Figure 8d, this problem is absent.

**6.3.** Phase Diagram of Multiblock Copolymer Adsorption. Using the values for the CAP, given in Table 1, one may construct a phase diagram showing the relative increase of the critical potential  $\epsilon_c(M)$  compared to that of a homopolymer against (inverse) block size M. This is one of the central results of the present study.

In Figure 9 one may see that the line of critical points, defining the region of adsorption, for both models is a steadily growing function of the inverse block size  $M^{-1}$ . Evidently, the theoretical result, eq 25, appears to be in good qualitative agreement with simulation data for the different models. As far as eq 25 comes as a result of scaling analysis, it can be verified only up to a factor of proportionality. As mentioned in section 2.1, the CAP of a homopolymer,  $\epsilon_c^h$ , is of the same order as that of the "renormalized" chain consisting of diblocks,  $E_c^h$ . Thus from a fit of the data points with the expression eq 25 one may actually determine  $E_c^h$ . So in the MA model one gets  $E_c^h = 3.306$  and for PERM  $E_c^h = 1.254$ , that is, one gets values which are two to four times larger than the respective CAP values of a homopolymer in both models.

**6.4. Random Copolymers.** In this section we examine the adsorption transition of random copolymers with quenched disorder and average percentage p of the A monomers. In addition to testing the scaling behavior, we also check to what extent one may employ the theory developed within approximation of "annealed disorder" for the description of the CAP properties. We performed Monte Carlo simulations for heterogeneous random copolymers of chains lengths 32, 64, 128, 256, and 512 (MA) and for  $64 \le N \le 2048$  (PERM) with different fraction of attractive monomers (p = 0.125, 0.25, 0.50, and 0.75).

It has been pointed out earlier<sup>15,16</sup> that the crossover exponent stays the same,  $\phi = 0.5$ , also in the case of random copolymers. Both simulation methods used in the present study demonstrate this in Figure 10 where qualitatively the observed picture is similar to that of Figure 7—small deviations in the attraction potential  $\epsilon$ , which was used when sampling the values of the order parameter *n*, manifest themselves in significant changes of the log–log slope  $\phi - 1$  from the expected value of -0.5. In Figure 11 we demonstrate that the scaling of the mena square gyration radius components, which we discussed before with regard to the multiblock copolymers, holds also for random copolymers with different composition *p*. Again, the value of  $\phi = 0.5$  gives best scaling results. Thus, it turns out that the composition affects only the value of the CAP  $\epsilon$ g.

In Figure 12 we present a plot of the critical point of adsorption against the fraction of attractive monomers. The full line corresponds to the theoretical prediction,<sup>12</sup> eq 39. Given that there are no fitting parameters in this equation, one finds a very good agreement between theoretical predictions and



Figure 11. log-log plots of the gyration radius components  $R_{gl}^2/N^{2\nu}$  and  $R_{g\perp}^2/N^{2\nu}$  vs  $kN^{\phi}$  with  $\nu = 0.588$  and  $\nu_2 = 3/4$  for random copolymers at different composition *p*.



**Figure 12.** CAP,  $\epsilon g$ , plotted vs the composition *p* for random copolymers. The curves give the best fit of eq 39,  $\epsilon g = \ln[(\exp \epsilon_c^h + p - 1)/p] \ge \epsilon_c^h$ . The critical points of adsorption for homopolymers are (a)  $\epsilon_c^h = 1.716$  (MA) and (b)  $\epsilon_c^h = 0.285$  (PERM). Symbols denote the CAP for multiblock copolymers with block size *M*.

simulation results as well as with very recent simulation results<sup>19</sup> which demonstrates the adsorption of random copolymers can be properly described within the scope of the annealed approximation. This confirms an earlier theoretical result derived in a somewhat different context (heteropolymer coil-globule transition) by Grosberg and Shakhnovich.<sup>23</sup> Figure 12 also indicates that this approximation breaks down for chains which are not random; <sup>19</sup> at 50% composition the CAPs of regular block copolymers are clearly off the theoretical prediction, eq 39. As far as polymer adsorption is greatly facilitated by the formation of trains of monomers on the substrate,<sup>19</sup> the larger the block size *M*, the lower the respective CAP  $\epsilon_c^M$  under the line, eq 39. No monomer trains are possible in the case of alternating chains which results in an  $\epsilon_c^{M=1} > \epsilon_c^p$ . Thus, from the position of the CAPs in Figure 12 one may conclude that the mean length of an A train on the substrate at p = 0.5 is close to 4.

## 7. Concluding Remarks

The main focus of the present investigation was aimed at the adsorption transition of random and regular multiblock copolymers on a rigid substrate. We have used two different models to establish an unambiguous picture of the adsorption transition and to test scaling predictions at criticality. The first one is an off-lattice coarse-grained bead-spring model of polymer chains which interact with a structureless surface by means of a contact potential, once an A monomer comes close enough to be captured by the adsorption potential. The second one deals with SAW on a cubic lattice by the pruned-enriched Rosenbluth method (PERM) which is very efficient, especially for very long polymer chains, and provides high accuracy of the simulation results at criticality. Notwithstanding their basic difference, both methods suggest a consistent picture of the adsorption of copolymers on a rigid substrate and confirm the theoretical predictions even though the particular numeric values of the critical adsorption potential (CAP) are model-specific and differ considerably.

As a central result of the present work, one should point out the phase diagram of regular multiblock adsorption which gives the increase of the critical adsorption potential  $\epsilon_c^M$  with decreasing length M of the adsorbing blocks. For very large block length,  $M^{-1} \rightarrow 0$ , we find that the CAP approaches systematically that of a homogeneous polymer. We demonstrate also that the phase diagram, derived from computer experiment within the framework of two different models, agrees well with the theoretical prediction based on scaling considerations.

The phase diagram for random copolymers with quenched disorder which gives the change in the critical adsorption potential,  $\epsilon g$ , with changing percentage of the sticking A monomers, p, is also determined from extensive computer simulations carried out with the two models. We observe perfect agreement with the theoretically predicted result which has been derived by treating the adsorption transition in terms of the "annealed disorder" approximation.

We show that 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 appears 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 homopolymers, regular multiblock polymers, or random polymers are concerned. Thus, the universality class of the adsorption transition of a heteropolymer is the same as that of a homopolymer.

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