# Macromolecules

### Effect of Chain Stiffness on the Adsorption Transition of Polymers

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**ABSTRACT:** Polymers grafted with one chain end to an impenetrable flat hard wall which attracts the monomers with a short-range adsorption potential (of strength  $\varepsilon$ ) are studied by large scale Monte Carlo simulations, using the pruned– enriched Rosenbluth method (PERM). Chain lengths up to N = 25600 steps are considered, and the intrinsic flexibility of the chain is varied via an energy penalty for nonzero bond angles,  $\varepsilon_b$ . Choosing  $q_b = \exp(-\varepsilon_b/k_BT)$  in the range from  $q_b = 1$  (fully flexible chains) to  $q_b = 0.005$  (rather stiff chains with a persistence length of about  $l_p = 52$  lattice spacings), the



adsorption transition is found to vary from about  $\varepsilon/k_BT_c \approx 0.286$  to  $\varepsilon/k_BT_c \approx 0.011$ , confirming the theoretical expectation that  $\varepsilon/k_BT_c \propto 1/l_p$  for large  $l_p$ . The simulation data are compatible with a continuous adsorption transition for all finite values of  $l_p$ , while in the rigid rod limit  $(l_p \rightarrow \infty)$  a first order transition seems to emerge. Scaling predictions and blob concepts on the structure of weakly adsorbed semiflexible polymers absorbed at interfaces are briefly discussed.

#### 1. INTRODUCTION

Adsorption of macromolecules onto surfaces and interfaces is of basic importance for creating polymeric layers, nanostructured soft materials, etc., and plays also a key role in processes involving biopolymers in a biological context. In addition, the interplay between the configurational entropy of the macromolecule (which is modified by the constraining interface) and the enthalpic gain due to adsorption is a challenging problem of statistical mechanics, and this aspect has found attention since a long time (e.g., refs 1-15), even if one restricts attention to neutral polymers in dilute solutions under good solvent conditions. Understanding this generic problem is of crucial importance before one can consider complications such as variation of solvent conditions (e.g., refs 15 and 16), adsorption of charged polymers (e.g. refs 18-20), etc.

While the overwhelming part of the (very rich!) theoretical literature on the subject has idealized the adsorbing macromolecules as fully flexible chains, it is well-known that intrinsic chain stiffness is a very important characteristic of most macromolecules,  $^{21-25}$  both for simple synthetic macromolecules like polyethylene or polystyrene, and biopolymers such as single- and double-stranded DNA. Consequently, there have been some attempts to consider the configurational statistics of semiflexible polymers near an adsorbing surface.  $^{26-41}$  However, all these approaches have some limitations: (i) in some studies the semiflexible polymers are modeled as a directed random walk or the continuum version thereof;  $^{26,29,32,37-39,41}$  existing computer simulations could explore only limited ranges of chain lengths and polymer stiffness;  $^{31,36}$  and some treatments rely on qualitative scaling arguments together with an approximate perturbation theory.  $^{33-35}$  Of course, some reservations about these studies are appropriate: e.g., it is now clearly established that in d = 2 dimensions, which is the proper situation to consider for a strongly adsorbed chain, excluded volume interactions are very important also for rather stiff polymers.<sup>42–45</sup> It has been shown that in d = 2 a direct crossover from rod-like behavior to self-avoiding walk-like behavior occurs when the contour length L of the chain significantly exceeds the persistence length  $l_v$ , and hence the popular Kratky–Porod (K–P) model<sup>46</sup> of wormlike chains should not be used in d = 2 at all.<sup>42,43</sup> At the adsorption transition, a grafted polymer changes its conformation from a threedimensional "mushroom" to a quasi-two-dimensional "pancake",<sup>3</sup> and the extent to which the K-P model can be used to describe the adsorption of semiflexible polymers hence needs to be clarified: in fact, this is one of the main aims of the present work. To avoid misconceptions, we stress that the terms "mushroom" and "pancake" refer to the average configuration of the segment cloud, where an orientational average around an axis perpendicular to the adsorbing surface in the grafting point has been taken. Instantaneous shapes of the chains will not exhibit any cylindrical symmetry, of course (just as the instantaneous shape of a random walk in d = 3 is not a sphere, but rather resembles a soap bar).

We also note that the conclusions of the existing studies on the adsorption transition of semiflexible chains are somewhat confusing or even contradictory. E.g., Burkhardt<sup>30</sup> finds that the adsorption transition is of first order while Birshtein et al.<sup>26</sup> and Khokhlov et al.<sup>29</sup> state it is second order, and Kuznetsov and Sung<sup>33–35</sup> propose a phase diagram where (in the limit of

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**Figure 1.** (a) Schematic log–log plot of the normalized mean square end-to-end distance  $\langle R^2 \rangle / (2l_pL)$  versus  $n_p = L/l_p$  (note that  $n_p = 2n_{kr} n_k$  being the number of Kuhn segments, if one has Gaussian chain statistics). The Kratky–Porod (K–P) model describes the crossover from rods ( $\langle R^2 \rangle = L^2$ ) to Gaussian coils ( $\langle R^2 \rangle = 2l_pL$ ). At  $n_p = n_p^* = (l_p/D)^2$  a smooth crossover from Gaussian to swollen coils occurs, as indicated. Ignoring prefactors of order unity, one has then  $\langle R^2 \rangle = 2l_p^2(D/l_p)^{2/5}n_p^{6/5}$  in this regime. (b) Schematic Kratky plot qLS(q) of the structure factor S(q) plotted versus the scaled wavenumber qL, on log–log scales. Four regimes occur: at small q the Guinier regime,  $S(q) = 1 - q^2 \langle R_g^2 \rangle / 3$ ,  $\langle R_g^2 \rangle$  being the mean square gyration radius of the polymer; for  $q > q_{max}$  with  $q_{max} \propto 1/(\langle R_g^2 \rangle)^{1/2}$  being the position of the maximum of the Kratky plot, one has a power law  $S(q) \propto q^{-1/\nu}$  (characteristic of swollen coils) crossing over at  $qR^* \approx 1$  to the power law of Gaussian coils ( $S(q) \propto q^{-2}$ ) and at still larger q (namely for  $ql_p > 1$ ) to rod-like scattering ( $S(q) \approx \pi/(Lq)$ ). Only the last two regimes are described accurately by the K–P model.

infinite chain length) one has both first order adsorption transitions (to a "pancake" with liquid-crystalline order) and second order transitions (to an isotropic "pancake"), depending on the ratio between persistence length  $(I_p)$  and the range of the adsorption potential. Recalling that, unlike the case of ideal chains considered in the textbooks,<sup>21–25</sup> the concept of a "persistence length" as a characterization of intrinsic stiffness of polymer chains is problematic,<sup>42,43,47</sup> it is clear that a proper analysis of the effects of chain stiffness on polymer adsorption is subtle.

One needs to realize that for semiflexible chains in d = 3dimensions the persistence length is also responsible for two crossovers in quantities characterizing the coil structure; such crossovers that are not present for completely flexible chains (Figure 1). The first crossover in the mean square end-to-end distance, from rods to Gaussian coils, is described by the K-P model, but when one takes excluded volume into account, this is not the whole story: when  $n_p = L/l_p$  becomes of the order of  $n_p^* = (l_p/D)^2$ , Flory theory<sup>48</sup> predicts a second crossover to swollen coil behavior, with  $\langle R^2 \rangle \propto n_p^{2\nu}$ , with the Flory exponent  $\nu = 3/5$ <sup>22</sup> Here the strength of the excluded volume interaction has been related to the effective thickness (cross-section diameter D) of the polymer chain.<sup>48</sup> (Remember that in d = 3dimensions the second virial coefficient  $v_2$  is simply proportional to the excluded volume, proportional to  $l_n^2 D$ , when one pictures the chain as a freely jointed chain of rods of length  $l_n$ and diameter D.) Note that for flexible chains under good solvent conditions,  $l_p$  is of the same order as the bond length  $l_b$ between subsequent effective monomers along the chain, and then in Figure 1a both the rod-like regime and the Gaussian plateau essentially disappear, and only the power law  $\langle R^2 \rangle \propto$  $n_p^{2\nu}$  survives, down to small values of  $n_p$ . For the case of stiff chains where stiffness is caused by thickness  $(l_p \propto D)$ , the Gaussian plateau may disappear, but the rod regime remains In d = 2 dimensions, however, irrespective of D one has always a direct crossover from rods to self-avoiding walks, but with  $\nu =$ 

 $\nu_2 = 3/4$ ,<sup>23–25</sup> when  $n_p$  is large. The rod–coil crossover at  $n_p = 1$  corresponds to a length scale  $l_p$ , and the crossover from Gaussian to swollen coils at  $n_p^*$  corresponds to a length scale  $R^* = l_p \sqrt{n_p^*} = l_p^2/D$  (prefactors of order unity are disregarded throughout). Of course, these length scales  $\langle R^2 \rangle^{1/2}$ ,  $R^*$ , and  $l_p$  can all be identified also from the scattering function of a semiflexible polymer (Figure 1b<sup>49</sup>). Hence it is an interesting problem to clarify the relation of these internal length scales to the thickness of the "pancake" that forms in the adsorption transition. This question will also be addressed in our study.

The outline of this paper is as follows: in the next section, we briefly recall the main theoretical predictions for the adsorption transition of flexible chains, and mention a few of the predictions for semiflexible chains in more detail. The third section gives a few comments on the model and simulation method, while the fourth section describes our results. The paper ends with a short summary.

## 2. SUMMARY ABOUT THEORETICAL CONCEPTS ON THE POLYMER ADSORPTION TRANSITION

We remark that Figure 1 can be interpreted in terms of a blob picture, with the length scale  $R^*$  being the radius of a blob: we have  $n_p$  segments of length  $l_p$  per blob, and Gaussian statistics prevail inside a blob. The chain can then be pictured as a self-avoiding walk of such blobs. Since the number of such blobs is  $n_p/n_p^*$ , one concludes

$$\langle R^2 \rangle \propto R^{*2} (n_p / n_p^*)^{2\nu}$$

$$= l_p^2 \left( \frac{D}{l_p} \right)^{2/5} n_p^{6/5}$$

$$= (l_p D)^{2/5} l_b^{6/5} N^{6/5}$$
(1)

where in the last step we have written the contour length  $L = l_p n_p = N l_b$  in terms of the number N of effective segments  $l_b$ .

In the adsorption transition, one relevant aspect is the range of the adsorption potential;<sup>17</sup> however, here we shall treat only the case of a strictly short-range contact potential, consistent with the choice of the lattice model used for the simulation (see next section) where an energy  $\varepsilon$  is won only if an effective monomer is situated in the surface plane.

The simplest case to consider by a phenomenological theory<sup>17</sup> is the case of fully flexible chains. For temperatures slightly below the adsorption temperature the chain is expected to form a quasi-two-dimensional "pancake" configuration, which has a thickness  $\xi$ . However, the area taken by the "pancake" is not uniformly filled by the *N* effective monomers; rather we expect a two-dimensional self-avoiding walk of "blobs" of diameter  $\xi$ . Inside a blob, we have statistics of self-avoiding walks in d = 3, and hence each blob contains *g* effective monomers, with  $g = (\xi/l_b)^{1/\nu}$ . Since each effective monomer must be in a blob, the number of blobs is  $n_{\text{blob}} = N/g = N(l_b/\xi)^{1/\nu}$ , while the size of the chain in the directions parallel to the surface is  $(\nu_2 = {}^3/_4)$  is the Flory exponent in d = 2 dimensions)

$$R_{g|l} \approx \xi n_{blob}^{\nu_2} = \xi N^{\nu_2} (l_b / \xi)^{\nu_2 / \nu} = l_b (l_b / \xi)^{(\nu_2 / \nu) - 1} N^{\nu_2}$$
(2)

The situation is analogous to the problem of confinement of a chain between two repulsive walls a distance  $\xi$  apart,<sup>50</sup> and just analogous to this case one can argue that there is a free energy cost of  $k_BT$  per blob, so the repulsive part of the free energy due to the confinement in the pancake is (in units of  $k_BT$ )

$$\mathcal{F}_{\rm rep} = n_{\rm blob} = N(l_b/\xi)^{1/\nu} \tag{3}$$

This repulsive part now is balanced by the gain in free energy due to the attractive surface potential  $^{17}$ 

$$\mathcal{F}_{att} = -c(T_c/T - 1)Nf_s \tag{4}$$

where *c* is a constant,  $T_c$  the critical temperature of the adsorption transition, and  $f_s$  the probability to find a monomer at the substrate surface. For  $T = T_c$  the number of monomers in contact with the surface is given by a power law, involving the crossover exponent  $\phi$ ,  $Nf_s \propto N^{\phi}$ .<sup>4,6</sup> By analogy, we can conclude for the chain of  $n_{\text{blob}}$  blobs containing *g* monomers that  $f_s \propto g^{\phi-1} = (\xi/l_b)^{(\phi-1)/\nu}$ . Hence, the phenomenological free energy expression becomes

$$\mathcal{F} = \mathcal{F}_{\text{rep}} + \mathcal{F}_{\text{att}} = N(l_b/\xi)^{1/\nu} - Nc \left(\frac{T_c}{T} - 1\right) (\xi/l_b)^{(\phi-1)/\nu}$$
(5)

Now the thickness  $\xi$  of the pancake follows from minimization of this free energy,  $\partial \mathcal{F} / \partial \xi = 0$ , as

$$\xi/l_b \propto (T_c/T - 1)^{-\nu/\phi} \tag{6}$$

For ideal Gaussian chains one has  $\nu = \phi = 1/2$  and hence  $\xi/l_b \propto (T_c/T - 1)^{-1}$  while the crossover exponent  $\phi$  in the excluded volume case is still not accurately known. The first Monte Carlo estimates<sup>4</sup> yielded  $\phi \approx 0.59$  while the current best estimates are significantly smaller<sup>14</sup> ( $\phi \approx 0.48$ ). In contrast,  $\nu$  is known much more precisely<sup>51</sup> ( $\nu \approx 0.588$ , rather than the Flory value  $\nu_F = 3/5$ ). Combining then eqs 2, 6 one obtains

$$R_{g\parallel}/l_b \propto (T_c/T - 1)^{(\nu_2 - \nu)/\phi} N^{\nu_2}, \quad N \to \infty$$
 (7)

and the number of monomers in contact with the wall, which is denoted as  $N_s$  in the following, becomes

$$N_s = Nf_s \propto N(T_c/T - 1)^{(1-\phi)/\phi}, \quad N \to \infty$$
(8)

Note that  $\xi$  can, ignoring again prefactors of order unity, be identified with the perpendicular gyration radius of the chain in the adsorbed regime,

$$R_{g\perp}/l_b \propto \xi/l_b \propto (T_c/T - 1)^{-\nu/\phi}, \quad N \to \infty$$
<sup>(9)</sup>

The relations eqs 7-9 were first derived on the basis of renormalization group calculations and complementing scaling arguments.<sup>4</sup> In fact, one can also consider similarly the crossover near  $T_c$  to the three-dimensional self-avoiding walk behavior for large but finite N,

$$R_{g||}/l_b = N^{\nu} \tilde{R}_{g||} \{ (T_c/T - 1) N^{\phi} \}$$
(10)

$$R_{g\perp}/I_b = N^{\nu} \tilde{R}_{g\perp} \{ (T_c/T - 1) N^{\phi} \}$$
(11)

$$N_{s} = N^{\phi} \tilde{N}_{s} \{ (T_{c}/T - 1) N^{\phi} \}$$
(12)

The scaling functions all reduce to nonzero constants for vanishing argument  $\kappa = (T_c/T - 1)N^{\phi} = 0$ , and behave for large positive arguments  $(T < T_c)$  as

$$\begin{split} \tilde{R}_{g\parallel}(\kappa) \propto \kappa^{(\nu_2 - \nu)/\phi}, \quad \tilde{R}_{g\perp}(\kappa) \propto \kappa^{-\nu/\phi}, \\ \tilde{N}_{s}(\kappa) \propto \kappa^{(1-\phi)/\phi} \end{split} \tag{13}$$

in order to reproduce eqs 7–9. Since  $\kappa^{\nu/\phi}$  can be just interpreted as the ratio of the free chain radius  $l_b N^{\nu}$  and the pancake thickness  $\xi$ , the scaling description of eqs 7-13 just means that all large lengths in the system are rescaled in terms of the blob size  $\xi$  as given in eq 6.

We now turn to a modification of this picture due to chain stiffness: recall that already in eq 2 it was implicitly used that for a free chain there was no other length scale than the chain radius  $l_b N^{\nu}$ , apart from the "microscopic" length  $l_b$ . As is obvious from eq 1, for semiflexible polymers this is not true.

A simple case results again if the chain is not extremely long but very stiff, such that  $n_p = N l_b / l_p$  does not exceed  $n_p^*$ . Then we conclude that for the weakly adsorbed case excluded volume effects are still negligible, and we simply can use a treatment analogous to eqs 2–13, but replacing  $l_b$  by  $l_p$ , N by  $n_p$ , and using mean field exponents  $\phi = \nu = 1/2$  but keep  $\nu_2 = 3/4$ , assuming that the adsorbed blobs that form the pancake remain self-avoiding. In this way one would predict

$$\xi/l_p \propto (T_c/T - 1)^{-1}, \quad R_{gll}/l_p \propto (T_c/T - 1)^{1/2} n_p^{3/4},$$

$$N_s \propto n_p (T_c/T - 1)$$
(14)

It is clear that the observability of this regime will be rather restricted, since we need to have  $\xi/l_p$  larger than one but  $n_p$  large enough so that  $\langle R_{g\perp}^2 \rangle$  no longer depends on *N*. It must be noted, however, that also the location of the adsorption transition itself shows a very interesting dependence on chain stiffness: mean field calculations show<sup>26,29,32</sup> that  $\varepsilon/k_{\rm B}T_c \propto 1/l_p$ , i.e., at a fixed value of  $\varepsilon$  we expect  $T_c \rightarrow \infty$  for  $l_p \rightarrow \infty$ . The obvious interpretation is that with increasing stiffness the entropy loss upon adsorption gets smaller, and therefore adsorption gets easier, as observed already in various studies.<sup>31,32,36</sup> It has been argued that for  $l_p \rightarrow \infty$ , the

adsorption of a rigid rod, the transition assumes the character of a first order transition.<sup>26,27</sup> However, we emphasize that the mean field theories<sup>26,29,32</sup> cannot make any useful predictions for the parallel linear dimension  $R_{\rm gll}$  of the adsorbed chains, irrespective of chain stiffness, since the Gaussian statistics invoked in the theories implies  $\nu_2 = 1/2$  as well.

When  $n_p \gg n_p^*$ , however, excluded volume is relevant on large length scales for the structure of mushrooms in the nonadsorbed regime and right at the adsorption transition, and eq 1 describes perpendicular and parallel linear dimensions of the chains also in this case. In order to discuss the weakly adsorbed regime, we note that for the case where the pancake thickness (or blob diameter) exceeds  $R^*$ , we must replace the relation  $\xi = l_k g^{\nu}$  by a relation motivated by eq 1, namely

$$\xi = (l_p D)^{1/5} l_b^{3/5} g^{3/5}, \quad n_{\text{blob}} = N/g = N \left[ \frac{(l_p D l_b^{3})^{1/5}}{\xi} \right]^{5/3}$$
(15)

Using again  $\mathcal{F}_{rep} = n_{blob}$  and comparing with eq 3 we see that the length  $l_b$  in eq 3 is replaced by a slightly larger length, namely  $(I_p D l_b^3)^{1/5}$ . Carrying through the further steps of this scaling analysis, we expect another crossover near the adsorption transition, when the length  $\xi$  (which very close to  $T_c$  is of the same order as  $(\langle R^2 \rangle)^{1/2}$  in eq 1) has decreased to  $\xi \approx R^*$ , since then inside of the blobs the excluded volume is no longer operative.

As long as one has blobs of size  $R^*$  or larger, which are essentially three-dimensional objects, it is clear that one still has many bonds in loops and hence the fraction of bonds that have parallel orientation to the wall is small, and the corresponding nematic order parameter that measures the fraction of bonds parallel to the surface still is small. On the other hand, for a very strongly adsorbed polymer most of the bonds will be in trains tightly bound to the substrate surface, and only a small fraction of bonds in loops is oriented differently. Kuznetsov and Sung<sup>33–35</sup> have presented various arguments to suggest that for  $N \rightarrow \infty$  these weakly and strongly adsorbed states are separated by a first order transition. However, we shall not go into the details of these arguments here.

#### 3. MODEL AND SIMULATION METHOD

Our model is the standard self-avoiding walk (SAW) on the simple cubic lattice, for a semi-infinite geometry with the plane z = 0 being the surface where a polymer is grafted with one chain end. Effective monomers are described by occupied lattice sites, connected by bonds of length  $l_b$ , equal to one lattice spacing, which henceforth is taken as our unit of length. Each site can be taken only once, to respect the excluded volume interaction.

There are two energy parameters in our model: every monomer in the surface plane z = 0 gains an adsorption energy  $-\varepsilon$  ( $\varepsilon > 0$ ), and the second energy parameter  $\varepsilon_b$  appears in the bending energy  $U_b = \varepsilon_b(1 - \cos \theta)$ , where  $\theta = 0, \pm 90^\circ$  is the angle between two subsequent bond vectors along the chain. The partition function then can be expressed in terms of the two Boltzmann factors  $q = \exp(\varepsilon/k_BT)$  and  $q_b = \exp(-\varepsilon_b/k_BT)$ as follows

$$Z_N(q, q_b) = \sum_{\text{config.}} C_{N, N_{\text{bend}}, N_s} q_b^{N_{\text{bend}}} q^{N_s}$$
(16)

where  $C_{N,N_{\text{bend}}N_s}$  is the total number of all configurations of a polymer chain of length N containing  $N_s$  monomers at the surface and  $N_{\text{bend}}$  kinks. This model is studied by Monte Carlo methods using the pruned–enriched Rosenbluth method (PERM).<sup>52,53</sup> Details on this algorithm and its efficient implementation have recently been extensively reviewed<sup>53</sup> and hence are omitted here.

The quantities that are analyzed in the following are the average number  $\langle N_s \rangle$  of monomers in the surface plane, components of the mean square gyration radius parallel  $(\langle R_{\rm g\parallel}^2 \rangle)$  and perpendicular  $(\langle R_{\rm g\perp}^2 \rangle)$  to the surface, and the local order parameter  $\zeta(k)$  that describes the adsorption of monomers along the chain, where k = 1, ..., N labels the monomers along the chain from the grafting site to the free chain end. We have defined  $\zeta(k)$  as

$$\zeta(k) = 1$$
, if  $z_k = 0$ ;  $\zeta(k) = 0$ , if  $z_k = 1, 2, ...$ 
(17)

where  $z_k$  is the *z*-coordinate of the *k*'th monomer (note that the lattice spacing is our unit of lengths).

In addition, the conformational properties of the partially or fully adsorbed chains have been analyzed in terms of the concept of dividing a chain up in loops, trains and tails,<sup>7</sup> see Figure 2. Of particular interest are then the fraction of



Figure 2. Schematic representation of the classification of a partially adsorbed mushroom in terms of loops, trains and tail. "Trains" are sequences of monomers adsorbed in the surface plane that are not interrupted by any loops. For simplicity, a two-dimensional system with a one-dimensional surface is sketched, but all actual data refer to three-dimensional systems with two-dimensional walls.

monomers in loops,  $\langle m_{\rm loop} \rangle / N$ , trains,  $\langle m_{\rm train} \rangle / N$ , and in the tail,  $\langle m_{\rm tail} \rangle / N$ , as well as the average lengths of trains  $\langle l_{\rm train} \rangle$ , loops  $\langle l_{\rm loop} \rangle$  and tails  $\langle l_{\rm tail} \rangle$ , and the total number of loops  $\langle n_{\rm loop} \rangle$ , trains  $\langle n_{\rm train} \rangle$ , and tails  $\langle n_{\rm tail} \rangle$  of a chain.

Next we define the average length of trains  $\langle l_{\text{train}} \rangle$ , loops  $\langle l_{\text{loop}} \rangle$ , and tails  $\langle l_{\text{tail}} \rangle$  in a chain

$$\langle l_{\rm train} \rangle = \langle m_{\rm train} / n_{\rm train} \rangle \tag{18}$$

$$\langle l_{\rm loop} \rangle = \langle m_{\rm loop} / n_{\rm loop} \rangle \tag{19}$$

and

$$\langle l_{\text{tail}} \rangle = \langle m_{\text{tail}} / n_{\text{tail}} \rangle \tag{20}$$

Since some of the theories raise the possibility of nematic order of the adsorbed chains (segments oriented predominantly parallel to the adsorbing surface), we shall study also an orientational order parameter defined as

$$\langle \eta \rangle = \left(\frac{1}{N} \sum_{i=1}^{N} 3\langle \cos^2 \alpha_i \rangle - 1\right)/2 \tag{21}$$



**Figure 3.** (a) Bond autocorrelation function  $\langle \cos \theta(s) \rangle$  plotted (on a logarithmic scale) versus *s* (on a linear scale), for  $q_b = 0.05$  and four values of *q*, as indicated. The limiting behavior of nongrafted semiflexible chains in d = 2 and d = 3 also is included. Fitting straight lines to the initial decay of these curves on the plots yielded the estimates  $l_p(q)$ , cf. eq 22. (b) Same as part a, but for  $q_b = 0.005$ . All data are for N = 25600. (c) Rescaled persistence length  $l_p(q)/l_p(q = 1.0)$  plotted versus  $T_c/T - 1$  for several values of  $q_b$ . Estimations of  $q_c = \exp(\varepsilon/k_B T_c)$  are listed in Table 1.

Here  $\alpha_i$  is the angle between the *i*th bond vector and the +*z*-axis. Remember that  $\eta = 0$  if the bond vectors are randomly oriented, while  $\eta = -1/2$  if all bonds are parallel to the adsorbing surface. For  $N \to \infty$ , a nonadsorbed mushroom is expected to exhibit perfect orientational disorder,  $\eta = 0$ . In any pancake of finite thickness, the fraction of bonds in trains contributes terms (-1/2) per such bond; and hence the average order parameter  $\langle \eta \rangle$  is always nonzero for  $T < T_c$  in the limit  $N \to \infty$ . However, if a sharp transition from weakly adsorbed to a strongly adsorbed state occurs,  $\langle \eta \rangle$  will exhibit a jump.

Finally, we shall also consider the bond orientational correlation function  $\langle \cos \theta(s) \rangle$ , where *s* labels the distance between the bonds along the chain contour (*i* = 1 being the bond at the grafting site, *s* = *j* − *i* with  $1 \le i, j \le N$ ). This bond orientational correlation will be used to estimate the persistence length from the initial decay,

$$\langle \cos \theta(s) \rangle = \exp(-sl_b/l_p), \quad s < l_p/l_b$$
 (22)

However, one interesting aspect of the problem is that the effect of the bending potential  $U_b$  depends very strongly on the dimensionality of space that is available for the polymer chain: for the same choice of  $\varepsilon_b$  the persistence length in d = 2dimensions is much larger than in d = 3. Consequently, when the chain gets adsorbed the effect of the bending potential gets more pronounced. Figure 3 shows typical data for  $\langle \cos \theta(s) \rangle$ versus s, for mushrooms interacting with an adsorbing surface. It is seen that the curves  $(\cos \theta(s))$  versus s indeed depend distinctly on the parameter  $q = \exp(\varepsilon/k_B T)$ , that characterizes the adsorption strength, in the region where the adsorption transition occurs. In particular, for rather stiff chains  $(q_b =$ 0.005) the data for q = 1.020 already fall completely on the curve for d = 2, while the data for q = 1.0107 for  $s \le 50$  still are close to the case d = 3. We also observe that the mushroom at a nonadsorbing surface (q = 1.00) always coincide with the behavior of the free three-dimensional chain: for such long chains as studied here grafting does not have a significant effect on  $\langle \cos \theta(s) \rangle$ .

In all cases we recognize significant curvature on the semilog plot of  $\langle \cos \theta(s) \rangle$  versus *s*: this flattening of the curves for large enough *s* is not an accident, but rather an indication that the asymptotic decay is not an exponential, but rather a power law.<sup>42,43,47,54</sup>

$$\langle \cos \theta(s) \rangle \propto s^{-\beta}, \quad \beta = 2(1-\nu) \approx 0.824 \ (d=3)$$
  
or  $1/2 \ (d=2)$  (23)

While we expect that for adsorbed chains ultimately the twodimensional exponent ( $\beta = 1/2$ ) will control the behavior for N  $\rightarrow \infty$ , it is clear that for finite N gradual crossovers must occur. These gradual crossovers will show up as "effective exponents" having values intermediate between  $\beta = 0.5$  and  $\beta = 0.824$ . However, such effective exponents lack any deep physical significance, and hence are not studied here. But we note that from the initial slope of  $\langle \cos \theta(s) \rangle$  versus s we can identify an effective persistence length  $l_p(q)$ , which gradually increases from the three-dimensional value  $l_p^{(3d)}$  to the two-dimensional value  $I_p^{(2d)}$  as the critical point  $T_c$  of the adsorption transition is crossed (Figure 3c). We expect that  $l_p(q) < l_p^{(2d)}$  as long as the average order parameter  $\overline{\zeta} = (1/N)\Sigma_k \zeta(k)$  is less than unity. Figure 3c shows numerical examples for this smooth crossover of the persistence length from three-dimensional to twodimensional behavior.

This "renormalization" of the persistence length  $I_p(q)$  with progressing adsorption has not been considered in the literature, to the best of our knowledge, and hence it has also been ignored in the theoretical arguments sketched in section 2. Actually, we expect that the situation is even more complicated, since a weakly adsorbed chain will exhibit an inhomogeneous stiffness: tails and loops will appear to be more flexible rather



**Figure 4.** Plot of the local adsorption order parameter  $\zeta(k)$  versus k/N for N = 25600, and for  $q_b = 0.05$  (a) and  $q_b = 0.005$  (b) including five values of q near  $q_c$  in each case, as indicated. Note that  $q_c(q_b = 0.05) \approx 1.0901$  and  $q_c(q_b = 0.005) \approx 1.01095$ , respectively.



**Figure 5.** Plot of  $\langle R_{g\perp}^2 \rangle / \langle R_{g\parallel}^2 \rangle$  versus N (on a logarithmic scale) for  $q_b = 0.4$  (a), 0.05 (b), and 0.01 (c). Several choices of q are included as indicated. (d)  $\langle R_{g\parallel}^2 \rangle / N^{2\nu_2} \sim const$  in the adsorbed regime  $(q > q_c)$  for  $q_b = 0.05$ .

than the trains which obey already the two-dimensional configurational statistics. Figure 4 corroborates this suggestion by presenting data for  $\zeta(k)$ : One sees that for stiff chains  $\zeta(k)$  depends on k/N strongly, implying that near the grafting point the chain is much stiffer than near the free end. It is clear that all these effects are not captured by descriptions based on the simple Kratky–Porod model.

The almost horizontal variation of  $\zeta(k)$  for weakly adsorbed chains in Figure 4a is understood from the fact that there occur many short loops and short trains, and only for k/N near unity there is a clear decrease due to the tail; for very stiff chains the tail affects a significant fraction of the chain even for N as large as N = 25600.

We also stress that the effects demonstrated in Figure 3 need to be accounted for in experiments where one extracts estimates of the persistence from electron microscopy or atomic force microscopy images of adsorbed semiflexible chains.

#### 4. SIMULATION RESULTS FOR THE ADSORPTION OF SEMIFLEXIBLE CHAINS

**4.1. Estimation of the Location of the Adsorption Transition.** In order to obtain a first orientation, at which values of q adsorption of the chains occurs, the ratio of the linear dimensions  $\langle R_{g\perp}^2 \rangle / \langle R_{g\parallel}^2 \rangle$  of the chains is analyzed as a function of N for various stiffnesses in Figure 5 using q as a parameter in the region where (from preliminary runs) we expect that adsorption occurs: theoretically, we expect that in the adsorbed case  $(T < T_c$  i.e.,  $q > q_c)$  for  $N \to \infty$  this ratio decreases, since eqs 10–13 imply

$$\langle R_{g\perp}^{2} \rangle / \langle R_{g\parallel}^{2} \rangle = \tilde{R}_{g\perp}^{2}(\kappa) / \tilde{R}_{g\parallel}^{2}(\kappa) \propto \kappa^{-\nu_{2}/\phi}, \quad \kappa \to \infty$$
(24)

On the other hand, for  $T > T_c$  and  $T = T_o$ , we expect that this ratio tends to two (different) universal constants.

Figure 5 now demonstrates that finite chain length effects on this ratio do depend on chain stiffness distinctly: for a rather flexible chain  $(q_b = 0.4)$  we observe that for short chains this ratio increases with N up to a flat maximum, reached around N  $\approx 10^3$ , while then curves for different q fan out, some decreasing from this maximum, while others slowly increase further (and hence exhibit no maximum at all). Thus, it is clear that chains with  $N \leq 10^3$  cannot yield accurate results on the location of the adsorption transition and its exponents, at least for the present model. This finding clearly casts some doubts on the reliability of some of the published estimates for similar



**Figure 6.** Ratio between the mean square gyration radius components perpendicular and parallel to the surface,  $\langle R_{g\perp}^2 \rangle \langle R_{g\parallel}^2 \rangle$  plotted vs  $T_c/T - 1$  for  $q_b = 0.4$  (a), 0.05 (b), and 0.01 (c), including four choices of N in each case, N = 3200, 6400, 12800, and 25600, as indicated. The estimates for  $k_B T_c/\varepsilon$  used in the plot are 1/ln  $q_c$  with  $q_c = 1.2810$  (a), 1.0904 (b), and 1.02140 (c), respectively. Part d shows the same data as in part b, but rescaled versus the variable  $(T_c/T - 1)N^{\phi}$  with  $\phi = 1/2$ .

models where rather short chains were used.<sup>4,5,12,13</sup> On the basis of Figure 5a, it hence is tempting to conclude that for q = 1.2812 the ratio still decreases for large *N*, while for  $q \le 1.2810$  it is still slightly increasing, so we might expect that  $q_c \approx 1.2811(1)$ .

For a moderately stiff chain  $(q_b = 0.05)$ , however, the behavior of this ratio is rather different: it decreases with N to reach a minimum near  $N \approx 10^2$ , then it increases and reaches a maximum only close to  $N = 10^4$ , for q = 1.0906, for instance. For q = 1.0903, however, the data generated seem to suggest that a horizontal plateau, indicative of the asymptotic behavior at  $T = T_{o}$  actually has been reached. Of course, the scaling description of eqs 10–13 implies also that the ratio  $\langle \tilde{R}_{q\perp}^2(0) \rangle /$  $\langle \tilde{R}_{e\parallel}^2(0) \rangle$  should be a universal constant, irrespective of nonuniversal parameters such as  $q_b$  and hence the persistence length. If we rely on Figure 5a, the plateau characterizing  $T = T_c$ should be near  $\langle R_{g\perp}^2 \rangle / \langle R_{g\parallel}^2 \rangle = 0.32$  rather than 0.24, which we would conclude from Figure 5b if  $q_c = 1.0903$ . This contradiction already shows that the judgment whether the asymptotic scaling regime was actually reached is a delicate matter, and the probable answer for the case  $q_b = 0.05$  is presumably negative, even chains with N = 25600 are too short. Analyzing other quantities, as discussed below, our best estimate actually is  $q_c(q_b = 0.05) = 1.0901$ , where clearly no plateau in  $\langle R_{g\perp}^2 \rangle / \langle R_{g\parallel}^2 \rangle$  is reached yet. However, in the adsorbed regime  $(q > q_c)$  the expected scaling behavior  $R_{g\parallel}^2 \propto 10^{-2}$  $N^{2\nu_2}$  is indeed seen (Figure 5c).

For the case of very stiff chains, such as for  $q_b = 0.01$  (Figure 5c), we see a monotonic decrease for  $q > q_{c^2}$  and a minimum for  $q < q_c$ . The value of the plateau, if this can be identified as a plateau really, is very small (0.06), strongly contradicting the conjecture that the plateau value is universal. However, it is plausible that for such stiff chains the effect of excluded volume still is too small to have strong effects for the adsorption transition, for chains with N = 25600. Already in the bulk such chains in d = 3 still showed only minor deviations from the Kratky–Porod description.<sup>42,43,55</sup> So the worst case scenario to

be considered is the possibility that what we take as a "plateau"" in Figure 5c at  $N = 10^4$  is only the analogue of the flat part in the minimum of Figure 5b at  $N = 10^2$ , and the true plateau occurs for much larger N. The best estimate for  $q_c$  in fact is 1.02143, for which the minimum in Figure 5c, has not been reached yet. To check these results, it is interesting to also examine the variation of the ratio  $\langle R_{g\perp}^2 \rangle / \langle R_{g\parallel}^2 \rangle$  with  $T_c/T - 1$ , including only rather large N ( $N \ge 3200$ ), Figure 6. One expects that these ratios should intersect at  $T_c/T - 1 = 0$ , of course. Again the data are compatible with this expectation, but it is clear that with increasing chain stiffness the judgment where the intersection occurs precisely gets more and more difficult. Figure 6d anticipates that despite the problems noted in Figure 5 that data are roughly compatible with the scaling description, eqs 10, 11.

Thus, it becomes very desirable to obtain an independent estimate of  $q_c$ . At this point, we recall that the partition function  $Z_N$  that we estimate with the PERM algorithm is expected to exhibit the following behavior<sup>23,51</sup> in the bulk { $\mu(q_b)$  is the fugacity of the chain;  $\mu(q_b = 1) = 0.21349098(5)$  in ref 14}:

$$Z_N(q_b) \propto [\mu(q_b)]^{-N} N^{\gamma-1}, \quad \gamma \approx 1.162 \ (d=3)$$
 (25)

while for a (nonadsorbed) mushroom we have 4,6,9,10,14

$$Z_N(q, q_b) \propto [\mu(q_b)]^{-N} N^{\gamma_1 - 1}, \quad \gamma_1 \approx 0.679, \quad N \to \infty$$
(26)

In contrast, for an adsorbed chain in a (quasi-twodimensional) pancake conformation the exponent  $\gamma_1$  gets replaced by the exactly known<sup>56,57</sup> two-dimensional value  $\gamma_2 =$ 43/32 and  $\mu$  now depends on *q* as well,

$$Z_N(q, q_b) \propto [\mu(q, q_b)]^{-N} N^{\gamma_2 - 1}, \quad N \to \infty$$
<sup>(27)</sup>

In this description, the adsorption transition is a point<sup>4,6</sup> where  $\mu$  still depends on  $q_b$  only, while  $\gamma_1$  takes the value<sup>14,58</sup>  $\gamma_1 = \gamma_1^p \approx 1.22 \pm 0.01$  at the so-called "special transition". For Gaussian chains, the values of these exponents simply are<sup>4,6</sup>

Article



**Figure 7.** Effective exponents  $\gamma_{1,\text{eff}}^{(1)}$  and  $\gamma_{1,\text{eff}}^{(2)}$  [computed from eqs 29, 30] plotted versus *N* (on a logarithmic scale) for *q* = 1, and for *q<sub>b</sub>* = 0.4 (a) and 0.005 (b). To estimate  $\mu(q_b)$ , the combination  $\ln Z_N(q_b) + N \ln \mu(q_b) + (1 - \gamma_1) \ln N$  is plotted vs *N* for *q* = 1, and for *q<sub>b</sub>* = 0.4 (c) and 0.005 (d). Three trial values of  $\mu$  are shown in each case (values of  $\mu(q_b)$  are chosen such that the shown curves become horizontal for large *N*).



**Figure 8.** Effective exponents  $\gamma_{1,\text{eff}}^{(2)}$  at the adsorption transition, (computed from eq 30, using the estimates of  $\mu(q_b)$  obtained in the similar way as shown in Figure 7), plotted versus N (on a logarithmic scale) for  $q_b = 0.4$  (a), 0.05 (b), and 0.01 (c); values of q are included in each case, as indicated. At  $q = q_o$  computed values of  $\gamma_{1,\text{eff}}^{(1)}$  using eq 29 are also included. Estimations of the critical point  $q_c$  and the exponent  $\gamma_1$  are pointed out by arrows.

$$\gamma = 1, \quad \gamma_1 = 1/2, \quad \gamma_1^{sp} = 1$$
 (28)

In order to derive estimations of  $\gamma_1$  from eq 26, it is useful to consider expressions such as (we omit here the argument  $q_b$ , for simplicity)

$$\gamma_{l,\text{eff}}^{(1)} = 1 + [4 \ln Z_N - 3 \ln Z_{N/3} - \ln Z_{3N}] / \ln 9$$
(29)

 $\gamma_{1,\text{eff}}^{(2)} = 1 + \{\ln[Z_{2N}\mu^{3N/2}/Z_{N/2}]\}/\ln 4.$ (30)

As a test of this method, Figure 7 shows the estimation of  $\gamma_1$ and  $\mu(q_b)$  for mushrooms (q = 1). Indeed, one finds  $\gamma_1$  being close to 0.68 for  $q_b = 0.4$ , while  $\gamma_1$  is close to the mean field value 1/2 for  $q_b = 0.005$ , because in the available regime of chain lengths excluded volume hardly matters for such stiff chains. As expected,  $\mu(q_b) \rightarrow 1$  for  $q_b \rightarrow 0$ , for the same reason. Next we turn to the estimation of  $q_c$  and  $\gamma_1^{\rm sp}$  (Figure 8). The best estimates for  $q_c$  are chosen such that  $\gamma_{1,\rm eff}^{(2)}$  becomes

and



Figure 9. Plot of  $\phi_{\text{eff}}$  as defined in eq 31 versus N (on a logarithmic scale) for  $q_b = 0.4$  (a), 0.05 (b), and 0.01 (c). Five values of q are included in each case, as indicated.



**Figure 10.** Average number of adsorbed monomers  $N_s$  relative to the fraction  $N^{\phi}$  expected at the adsorption transition plotted versus N (on a logarithmic scale) for  $q_b = 0.4$  (a), 0.05 (b), and 0.01 (c). The effective values of the crossover exponent  $\phi$  used are  $\phi = 0.495$  (a), 0.47 (b), and 0.88 (c). Several choices of q are included, as indicated.

independent of N for large N. The resulting estimates for  $q_c$  are reasonably well consistent with the estimates obtained from the ratio of the linear dimensions (Figure 5). We note that the asymptotic region in Figure 8 seems to be reached for N > 200in the case  $q_b = 0.4$ , but N > 1000 for  $q_b = 0.05$  and still larger Nare required for  $q_b = 0.01$ . Qualitatively, this observation can be accounted for by the fact that the asymptotic behavior can only be observed for  $N > N^* = l_p n^*$ , and  $N^*(q_b)$  strongly increases with increasing stiffness. From the analysis of free (nongrafted) chains it was found<sup>49</sup> that  $N^*(q_b = 0.05) = 180$  while  $N^*(q_b =$ 0.01) = 9000. If these estimates are reliable, one must expect that for  $q_b \leq 0.01$  the asymptotic regime where excluded volume effects dominate has hardly been reached. While in the case of nonadsorbed mushrooms we can clearly see that the estimates for  $\gamma_1$  for N > 1000 settle down at a value close to the value for Gaussian chains,  $\gamma_1 = \frac{1}{2}$  (eq 28), for rather stiff chains (Figure 7b), at the adsorption transition data are compatible with the Gaussian value  $\gamma_1^{sp} = 1$  only for the rod-like regime, N < 100 (Figure 8c). We note that for nonreversal random walks, which are known to obey the Gaussian statistics, the exponents  $\gamma_1 = \frac{1}{2}$  and  $\gamma_1^{sp} = 1$  have been verified straightforwardly for rather short chains already ( $20 \le N \le 100$ ).<sup>4</sup>

Table 1. Estimations of the Adsorption Transition Point  $q_c$  (Figures 5, 8, and 9), the Crossover Exponent  $\phi$ , the Surface Entropic Exponent  $\gamma_1^{sp}$ , and the Persistence Length for the Semiflexible Polymer Chains with One Chain End Grafted on a Surface and in the Bulk,  $l_p(q = 1)$  and  $l_p(\text{bulk})$ , Respectively

$q_b$	0.005	0.01	0.02	0.03	0.05	0.10	0.20	0.40	1.0
$q_c(R_\perp^2/R_\parallel^2)$	1.010 90	1.021 40	1.0410	1.058 95	1.0904	1.1497	1.2196	1.2810	1.3307
$q_c(\gamma_1^s)$	1.010 95	1.021 43	1.0409	1.0587	1.0901	1.1495	1.2195	1.2809	1.3307
$q_c(\phi)$	1.010 97	1.021 48	1.0410	1.0588	1.0901	1.1495	1.2195	1.2810	1.3308
$\phi$	0.97	0.88	0.61	0.51	0.47	0.49	0.50	0.495	0.483
$\gamma_1^{sp}$	1.82	1.63	1.21	1.14	1.18	1.228	1.23	1.23	1.224
$l_p(q=1)$	52.60	26.80	13.91	9.54	5.92	3.34	2.00	1.13	0.68
$l_p$ (bulk)	52.61	26.87	13.93	9.54	5.96	3.35	2.05	1.13	0.68



**Figure 11.** Fraction of monomers in trains, loops, and tails,  $\langle m_{\text{train}} \rangle / N$ ,  $\langle m_{\text{loop}} \rangle / N$ , and  $\langle m_{\text{trail}} \rangle / N$ , respectively, plotted versus  $T_c/T - 1$  for  $q_b = 0.4$  (a),  $q_b = 0.05$  (b), and  $q_b = 0.005$  (c). Fraction of monomers in trains,  $\langle m_{\text{train}} \rangle / N$  for plotted versus  $T_c/T - 1$  (d), and  $(q - q_c)I_p(q, q_b)$  (e) several choices of  $q_{b}$ , as indicated. In parts a-d, data are for chains of length N = 25600. In part e, chain lengths N are chosen such that  $n_p = N/I_p(q, q_b) = 210$ . The abscissa variable  $(q - q_c)I_p$  in part e was used since  $(q - q_c)I_p \approx (T_c/T - 1)(\varepsilon I_p/k_BT_c)$  for stiff chains and  $\varepsilon I_p/k_BT_c$  tends to a constant.

A third method to locate  $q_c$  is based on eq 12, making use of the fact that the scaling function  $\tilde{N}_s(\kappa)$  for small  $\kappa = (T_c/T - 1)$  $N^{\phi}$  is a regular function of  $\kappa$ , we hence consider the function

$$\phi_{\rm eff}(N, q) = \ln[N_s(2N, q)/N_s(N/2, q)]/\ln 4$$
(31)

since with the help of eq 12 this becomes for  $|T_c/T - 1|N^{\phi} \ll 1$ 

$$\phi_{\rm eff}(N, q) \approx \phi + const(T_c/T - 1)N^{\phi} + \cdots$$
 (32)

Figure 9 shows that for relatively flexible chains we obtain results compatible with a universal value of  $\phi$  near  $\phi = 0.48$ , but for  $q_b \leq 0.01$  clearly a reliable value can no longer be extracted. From Figure 1, we can conclude that for very long semiflexible

chains we can expect for both exponents right at the adsorption transition,  $\gamma_{l,\text{eff}}^{p}$  and  $\phi_{\text{eff}}$  three distinct regimes: a regime characteristic for the adsorption of rods for  $N \leq l_p/l_b$ , a regime characteristic for the adsorption of Gaussian coils for  $l_p/l_b \leq N \leq N^* (= l_p^{-3}/l_b^{-2})$ , and a regime where the adsorption behavior characteristic of chains with excluded volume behavior prevails ( $N > N^*$ ). Apart from the fact that the behavior is difficult to analyze since the crossovers are smooth, we must also take into account that the behavior is more complicated since the location of the adsorption of rods occurs already as soon as  $\varepsilon > 0$ , while in the other cases  $\varepsilon/k_BT$  has to

2505



**Figure 12.** Fraction of monomers in loops  $\langle m_{loop} \rangle / N$  plotted versus  $T_c/T - 1$  for  $q_b = 0.05$  (a) and 0.005 (b) and plotted versus  $(q - q_c)I_p(q, q_b)$  for chains of length N = 25600 and several choices of  $q_b$ , as indicated (c). In parts a and b, four chain lengths N = 400, 1600, 6400, and 25600 are included, as indicated.



**Figure 13.** Average length of trains in a chain,  $\langle l_{\text{train}} \rangle$ , plotted versus  $T_c/T - 1$  for  $q_b = 0.05$  (a) and 0.005 (b). Arrows in (b) indicate the trivial limiting values  $\langle l_{\text{train}} \rangle = N$  for fully adsorbed chains where all monomers are in a single train. Average length of loops in a chain,  $\langle l_{\text{loop}} \rangle$ , plotted versus  $T_c/T - 1$  for  $q_b = 0.05$  (c) and  $q_b = 0.005$  (d). In each case four choices of N are included, N = 400, 1600, 6400, and 25600, as indicated.

exceed a threshold  $\varepsilon/k_BT_c$ . For adsorption of rods on the simple cubic lattice we do not expect any power law factor in the partition function, and hence  $\gamma_1 = \gamma_1^{sp} = 1$  for rods. Figures 7 and 8 are compatible with this assertion, considering that  $l_p(q_b = 0.01) \approx 27$  and  $l_p(q_b = 0.005) \approx 52$ . Having obtained an estimate of  $\phi$ , one can perform a consistency check, plotting  $N_s/N^{\phi}$  vs N at various values of q: for  $q = q_c$  one expects a horizontal plateau for large N. Figure 10 shows that for flexible chains indeed the data settle down to a plateau if  $N \approx 400$  or larger, while for stiffer chains (e.g.,  $q_b = 0.05$ ) the plateau only starts at about N = 2000. For very stiff chains ( $q_b = 0.01$ ) we have used an effective crossover exponent  $\phi_{\text{eff}} = 0.88$ , motivated

by Figure 9c and the expectation that for  $q_b \rightarrow 0$  the adsorption transition becomes first order. At this point we recall the suggestion by Causo et al.<sup>59</sup> that first order adsorption transitions still are described by eq 12 but with  $\phi = 1$ . The adsorption transition point  $q_c$  determined by the gyration radii (Figure 6), the surface entropic exponent  $\gamma_1^{sp}$  referred to the partition sum (Figure 8), and the crossover exponent  $\phi$ referred to the number of surface contacts (Figure 9) at  $q = q_c$ , and the persistence length  $l_p$  determined by the bond orientational correlation function (Figure 3) are listed in Table 1 for several values of  $q_b$ .



**Figure 14.** Average length of tails per monomer in a chain,  $\langle l_{tail} \rangle / N$ , plotted versus  $T_c/T - 1$  for  $q_b = 0.4$  (a), 0.05 (b), and 0.005 (c), and plotted versus  $(q - q_c)l_p(q, q_b)$  for chains of length N = 25600 and several choices of  $q_b$ , as indicated (d). In parts a–c, four values of N are shown, N = 400, 1600, 6400, and 25600, as indicated.

4.2. Structural Properties of Adsorbed Semiflexible Chains: Loops, Trains, and Tails. We start by discussing the fractions of monomers in trains, loops and tails, Figure 11. It is remarkable that for flexible chains near the adsorption transition there are almost no monomers in trains, and only the fraction of monomers in loops grows on expense of the monomers in the tail. Conversely, for moderately stiff chains we do observe for  $T < T_c$  a continuous growth of  $\langle m_{\text{train}} \rangle$ , and  $\langle m_{\rm loop} \rangle$  reaches a maximum for T slightly smaller than  $T_o$  while in this regime there now are hardly any monomers in the tail. For rather stiff chains (such as  $q_b = 0.005$ , Figure 11c) we observe that for  $T > T_c$  almost all monomers are in the tail, while for  $T < T_c$  almost all monomers are in trains: only for T very near  $T_c$  do we find some monomers in loops. For  $q_b =$ 0.005, the maximum of  $\langle m_{
m loop} 
angle / N$  is almost an order of magnitude smaller than the maximum value reached for  $q_b$  = 0.05. Plotting  $\langle m_{\text{train}} \rangle / N$  versus  $T_c / T - 1$  for different stiffness at our largest chain length shows that the adsorption transition gets much sharper with increasing stiffness (Figure 11d). Only in the nonadsorbed regime (Figure 11e) emerges a simple scaling ruled by the persistence length at the same  $n_p = N/l_p(q, q_h).$ 

It is also interesting, of course, to study how this behavior develops with increasing chain length (Figure 12). While the height of the peak of  $\langle m_{loop} \rangle$  near  $T = T_c$  for moderately stiff chains grows rather gradually (Figure 12a), for rather stiff chains this growth is quite rapid (Figure 12b). In the nonadsorbed regime (Figure 12c) a simple scaling ruled by the persistence length only remains for flexible and moderately stiff chains. Also when one considers the average length of loops and trains (Figure 13), one finds that for moderately stiff chains ( $q_b = 0.05$ , Figure 13a) the train length increases with decreasing T and it remains the same as chain lengths are large enough at fixed temperature T (a master curve is seen). Note that the monotonous behavior observed in Figure 13a is similar to the behavior observed for flexible chains ( $q_b = 0.05$ , [not shown]) for all chain lengths. For stiff chains ( $q_b = 0.005$ , Figure 13b) near  $T = T_{cr}$  the slope  $d\langle l_{\text{train}} \rangle / dT$  increases rapidly with *N*. In the regime where the chain is strongly adsorbed the curves reach a plateau,  $\langle l_{\text{train}} \rangle \approx N$ , there is a single train containing (almost) all monomers. Only in the nonadsorbed regime we observe that the data for large enough *N* fall on a master curve. Also with respect to the length of loops  $\langle l_{\text{loop}} \rangle$ , we note very characteristic differences: for sufficiently large *N*, the loop length always develops a maximum in the vicinity of  $T_{cr}$ . A master curve for large enough *N* is only observed in the adsorbed regime and moderate stiffness (we expect that for  $q_b =$ 0.005 much longer chains would be required to obtain a master curve as well).

We find that the average length of tails per monomer in a chain (Figure 14) qualifies as another criterion to estimate the location of the adsorption transition: we find that  $\langle l_{tail} \rangle / N$  is monotonically increasing with N for  $T > T_c$ , while for  $T < T_c$ this quantity is monotonically decreasing with N. Thus, in the limit  $N \to \infty$  almost all monomers belong to the tail for  $T > T_{cl}$ the fraction of monomers in loops and trains is negligibly small, consistent with observation (Figure 13). In contrast, for  $T < T_c$ for  $N \rightarrow \infty$  the fraction of monomers in the tails is negligible (remember that per definition there can only be at most one tail, Figure 2, and hence  $\langle l_{\text{tail}} \rangle = \langle m_{\text{tail}} \rangle$ , of course). For flexible chains,  $q_b = 0.4$ , the data clearly suggest that the curves for  $\langle l_{\rm tail} \rangle / N$  versus q intersect at a universal point  $\langle l_{\text{tail}} \rangle / N = \langle m_{\text{tail}} \rangle / N \approx 0.5$ , however, for  $q_b = 0.05$  there is clearly some spread of the intersections, while for  $q_b = 0.005$  the data again are compatible with a unique intersection, but at a smaller value,  $\langle l_{tail} \rangle / N \approx 0.3$ . It is tempting to speculatively attribute this change of behavior to a crossover of a second order adsorption transition for flexible chains to a first order transition in the limit  $l_p \rightarrow \infty$ . Figure 14d shows that the average length of tails per monomer,  $\langle l_{\rm tail} 
angle / N$  converges to a master curve for semiflexible chains (but not the flexible ones) when plotted as a function of  $(q - q_c)l_p(q, q_b)$ .



**Figure 15.** Rescaled average length of loops in a chain,  $\langle l_{loop} \rangle / (2l_p(q, q_b))$  (a), and rescaled average length of trains in a chain,  $\langle l_{train} \rangle / (2l_p(q, q_b))$  (b), plotted versus  $T/T_c$  for N = 25600 and  $q_b = 0.4$ , 0.2, 0.1, 0.05, 0.03, 0.02, 0.01, and 0.005 from top to bottom in part a, but from bottom to top in part b.



**Figure 16.** Average number of trains, loops and tails ( $\langle n_{\text{train}} \rangle$ ,  $\langle n_{\text{loop}} \rangle$ , and  $\langle n_{\text{tail}} \rangle$ ) plotted versus  $T_c/T - 1$  for N = 25600 and  $q_b = 0.05$  (a) and  $q_b = 0.005$  (b). Note the logarithmic scales of the ordinate axis in part a. (c) Average number of trains  $\langle n_{\text{train}} \rangle$  plotted versus  $T_c/T - 1$  for  $q_b = 0.01$  and for four different choices of N, as indicated. (d) Average number of tails  $\langle n_{\text{tail}} \rangle$  plotted versus  $(q - q_c)I_p(q, q_b)$  for N = 25600 and several choices of  $q_b$ , as indicated.

At this point it is also interesting to contrast the different behavior of  $\langle m_{\rm loop} \rangle$  and  $\langle l_{\rm loop} \rangle$  for  $T < T_c$  (Figure 12a,b and Figure 13c,d): while  $\langle m_{\text{loop}} \rangle / N$  for  $T < T_c$  converges to a limiting finite value with increasing N from below, the behavior of  $\langle l_{loop} \rangle / 2l_p$  shows a monotonic increase with temperature T (Figure 15a). The length of trains is monotonically decreasing as  $T \to T_c$  (Figure 15b). We have normalized both  $\langle l_{loop} \rangle$  and  $\langle l_{\text{train}} \rangle$  with  $2l_p$  here, since then our results can be compared to analogous plots of Khokhlov et al.<sup>29</sup> for the case without excluded volume, where qualitatively similar trends are observed. We note that at fixed  $T/T_c$  the length of trains  $\langle l_{\rm train} \rangle / 2 l_p$  increases very strongly with increasing stiffness, so there is no simple rescaling with the persistence length. Actually for  $T \to T_c$  we expect that  $\langle l_{\text{loop}} \rangle \to \infty$  for infinitely long chains, which is not seen. The reason for this fact, namely that for N = 25600 and stiff chains the asymptotic regime has not been reached, becomes clear when we examine the numbers of trains, loops and tails (Figure 16): For flexible [not shown] and semiflexible chains we typically find (for N = 25600) one tail and  $\langle n_{\rm loop} \rangle$  increases from about 10 to about 100 as T decreases from  $T_c$  to smaller values. The number of trains exceeds the

number of loops by unity, if a tail occurs (only if the free chain end is in a loop but also occurs at the surface z = 0, there is no tail, and then  $n_{\text{loop}} = n_{\text{train}}$ , cf. Figure 2).) However, for  $q_b =$ 0.005 the behavior for N = 25600 is rather different (Figure 16b): For  $T > T_{o}$  there are essentially no loops, so the chain conformation is composed from a train plus a tail; for  $T < T_{o}$ there are typically one or two trains (and at most one loop). However, in the thermodynamic limit we do expect that both  $\langle n_{\rm loop} \rangle$  and  $\langle n_{\rm train} \rangle$  increase proportional to N; clearly this limit is far beyond reach for our methods, however. For somewhat larger values of  $q_b$  (such as  $q_b = 0.01$ ) we can see that  $\langle n_{\text{train}} \rangle$ with increasing N starts to increase distinctly, however (Figure 16c). Figure 16d shows that the number of tails  $\langle n_{\text{tail}} \rangle$ converges to a master curve for semiflexible chains (but not the flexible ones) when plotted as a function of  $(q-q_{\rm r})l_{\rm p}(q,q_{\rm h}).$ 

Article

**4.3. Orientational Order Parameter and Its Distribution Function.** Since in the literature the possibility of transitions between phases of adsorbed chains with essentially no orientational order to phases with order parameter close to  $\langle \eta \rangle = -\frac{1}{2}$  (all bonds being oriented parallel to the adsorbing surface) has been raised,<sup>33–35</sup> it is of great interest to investigate



**Figure 17.** Average orientational order parameter  $\langle \eta \rangle$  plotted versus  $T_c/T - 1$  for  $q_b = 0.4$  (a), 0.05 (b) and 0.005 (c), including data for four chain lengths N = 3200, 6400, 12800, and 25600 in each case, as indicated. Part (d) shows the gradual crossover from the behavior characteristic of a second order adsorption transition toward a first order transition with increasing stiffness, showing data for N = 25600 but different  $q_b$  versus  $(q - q_c)I_p(q, q_b)$ . Note that for  $q_b \leq 0.02$  the curves no longer get steeper, since the finite size rounding gets more pronounced (the effective number of Kuhn segments  $N/(2I_p(q, q_b))$  decreases with decreasing  $q_b$ ).



**Figure 18.** Distribution function  $P(\eta)$  of the orientational order parameter  $\eta$  for N = 25600 plotted vs  $\eta$  for  $q_b = 0.05$  (a) and  $q_b = 0.005$  (b). Several values of q are shown in each case, as indicated.

the behavior of the orientational order parameter  $\langle \eta \rangle$  {eq 21} for our model (Figure 17). It is clear that the adsorbing surface does create some bias to orient bonds parallel to the surface, and so  $|\langle n \rangle|$  always differs somewhat from zero, but one sees that for flexible chains (Figure 17a) in the transition region this order parameter is extremely small and decreases with increasing chain length. Only when the thickness of the adsorbed layer is already small (as is the case in Figure 17b) we can see that  $\langle \eta \rangle$  converges toward N-independent nonzero and nontrivial values. Just as the density of monomers in the "pancake" increases gradually with the distance  $T_c/T - 1$  from the adsorption transition point for  $N \to \infty$ , also  $|\langle \eta \rangle|$  increases gradually from zero (at  $T = T_c$ ) but reaches the saturation value  $|\langle \eta \rangle| = 1/2$  only far below the adsorption transition temperature, where (for  $N \to \infty$ ) all monomers belong to a single train. For  $q_h = 0.05$  (and larger) our data clearly rule out a first order transition between a weakly adsorbed and a strongly adsorbed phase, which would show up as a jump (rounded by finite size) in the  $\langle \eta \rangle$  vs  $T_c/T - 1$  curve. For rather stiff chains (such as  $q_b = 0.005$ , Figure 17c) the transition toward orientational order is much more abrupt, however, and becomes sharper with increasing *N*, reminiscent of a finite-size rounded first-order transition, but it is a single transition, from the mushroom to the pancake. The gradual crossover from the behavior characteristic of a second order adsorption transition toward a first order transition with increasing stiffness is presented in the plot of  $\langle \eta \rangle$  versus  $(q - q_c)I_p(q, q_b)$  (Figure 17d).

We have also checked that near the adsorption transition the nonzero value of the orientational order parameter  $\eta$  is entirely due to the bonds belonging to trains (which trivially have  $\eta = -1/2$ ) while the average value of  $\eta$  for bonds in the tail and loops is  $\eta = 0$ , for large *N*. This fact is corroborated by examining the linear dimension of loops: e.g., for  $q_b = 0.01$ , q = 1.0215 (where  $\langle \eta \rangle \approx -0.2$ ) we find that  $(\langle R_g^2(I_{\text{loop}})_{\perp} \rangle / \langle R_g^2(I_{\text{loop}})_{\parallel} \rangle)^{1/2} \approx 0.5 \pm 0.2$ ; this implies that the loops have a random self-avoiding walk like structure, and should not be described as "hairpins", as done in the literature.<sup>29</sup>

Of course, in view of the behavior of trains, loops and tails (Figure 16) this result cannot come as a surprise: basically the



**Figure 19.** Distribution function  $P(m_{\text{train}}/N)$  as a function of  $m_{\text{train}}/N$  for N = 25600 and three choices of  $q_b$ :  $q_b = 0.4$  (a), 0.05 (b), and 0.005 (c). Several choices of q are included in each case, as indicated. Note the different abscissa scales.



**Figure 20.** Distribution function  $P(m_{loop}/N)$  versus  $m_{loop}/N$  for  $q_b = 0.4$  (a) and  $q_b = 0.005$  (b). All data are for N = 25600, and several choices of q are included, as indicated. Parts c and d present distributions of  $P(l_{loop})$  vs  $l_{loop}/N$  for  $q_b = 0.01$  (c) and 0.005 (d), as log-log plots, to indicate that at  $q_c$  (see Table 1) a power-law behavior occurs, as shown by the indicated straight lines.

chain behaves near the transition like a two-state model, being composed from a single train (of length  $I_{\text{train}}$ ) and a tail (or loop), respectively: while for  $T > T_c$  the length of the train is very short (Figure 13b), and almost all monomers are in the tail (Figure 14c), no loop being present as well, for  $T < T_c$  both the length of loop (if one is present) and the length of the tail (if one is present) get very small in comparison with the length of the single train (or two trains). At the transition, the lengths of the train and the tail (and/or loop) can fluctuate very easily and hence very strongly, there is no free energy barrier hindering the adsorption of a further part of the tail that then becomes part of the train, for instance. As a consequence, the distribution function of  $P(\eta)$  for  $q_b \rightarrow 0$  becomes very anomalous: While for continuous adsorption transitions  $P(\eta)$  is a Gaussian (Figure 18a), whose center gradually shifts to more negative values as q increases, for very stiff chains (such as for the case  $q_b = 0.005$ , see Figure 18b) the behavior is different: the distribution function  $P(\eta)$  develops a strongly non-Gaussian shape,with a "tail" extending from the peak position deeply into the region of strongly negative values (see the curve for q = 1.0106), while right at the transition ( $q \approx 1.0109$ ) the distribution is essentially flat over a regime from  $\eta \approx -0.15$  to  $\eta \approx -0.45$  (Figure 18b). Then, for still larger q (e.g., q = 1.0110), the distribution now has a peak near  $\eta = -0.48$ , but a tail still extends out to  $\eta \approx 0.1$ . Only for distinctly larger q (q = 1.0112 or larger) this tail diminishes.

This behavior seen in Figure 18b can be tentatively interpreted as a rounded first-order transition between a state



**Figure 21.** Plots of the adsorption transition point ln  $q_c$  (a) and the inverse of Kuhn length  $l_k^{-1}$  (b) versus the bending factor  $q_b$ . Here the threedimensional persistence length  $l_p$  was used to compute  $l_k$  ( $l_k = 2l_p$ ). Two predicted functions, eqs 33 and 34, in part a, and  $(1 + 1/(2q_b))^{-1}$  given in ref 29 are shown for the comparison, as indicated.

without orientational order ( $\eta = 0$  in the limit where first  $N \rightarrow \infty$  is taken and then  $q_b \rightarrow 0$ ) to a state with orientational order ( $\eta = -0.5$ ). However, unlike standard first-order transitions, the distribution in the system with finite N is not a double-Gaussian distribution, with two Gaussians centered at the two competing states, separated by a minimum in between; such a minimum would only occur if in the intermediate situation of phase coexistence between the two competing phases a free energy cost due to an interface separating the phases would occur. This is not the case here, the "interface" between the train and the tail is just a single bond from the last monomer of the train to the first monomer of the tail: this bond can be shifted along the chain with no free energy cost for  $q = q_c$ .

The situation is qualitatively similar to "phase coexistence" in the problem of force-induced desorption of an adsorbed chain.<sup>20</sup> Restricting the approach to Gaussian chains without excluded volume, the corresponding behavior could be described by the exact calculation. While for the present problem the transition point  $q_c(q_b)$  can also be computed exactly if excluded volume is ignored,<sup>26</sup> we are not aware of an analysis of  $P(\eta)$  in this framework.

Of course, it is possible to draw such conclusions about the gradual change of the nature of the adsorption transition from second-order like for flexible chains to first-order like for stiff chains directly from the corresponding distribution function of trains and loops and tails as well. As an example, Figure 19 presents distribution functions  $P(m_{\text{train}})$  of  $m_{\text{train}}$ . This distribution both for  $q_b = 0.4$  and 0.05 is characterized by a single peak, whose position gradually shifts as q is varied. However, for  $q_b = 0.005$  the behavior is qualitatively different: Now distributions develop tails extending over the full interval  $0 < m_{\text{train}}/N < 1$ , and right at the transition (near q = 1.0109) an almost horizontal plateau develops. In contrast, the distribution function  $P(m_{loop})$  is extremely broad at a continuous adsorption transition (Figure 20a) but exponentially decaying for the rounded first-order transition (Figure 20b). It is also interesting that for the distribution  $P(l_{loop})$  of the loop length  $l_{loop}$  at  $q_c$  a power law emerges (Figure 20c,d). Understanding this behavior in full detail must be left as a challenge for future work.

As a last point of this section, we tentatively discuss the question whether the change of the order of the adsorption transition (in the limit  $N \to \infty$ ) occurs for  $q_b \to 0$  only, or whether a tricritical point occurs at the transition line  $q_c(q_b)$  at some nontrivial value  $q_b$ . For this purpose, we compare our results for  $q_c(q_b)$  with the function of Birshtein et al.<sup>26</sup> recast for a simple Gaussian chain by Van der Linden at al.<sup>31</sup> in the form (eq 15 of ref 32):

$$\chi^{cr} = C \ln[(l_k + (l_k^2 + 4)^{1/2})/(2l_k + 2)]$$
(33)

where  $l_k = 2l_p$  is the Kuhn length, and in the normalization of energy parameters used in ref.<sup>32</sup> the constant C = 6. We find that our data for  $q_c(q_b)$  can be fitted quantitatively by eq 33 when ln  $q_c$  is identified with  $-\chi^{cr}$ , using C = 1.2 (Figure 21a). However, in eq 33 and in the corresponding function included in Figure 21a, the actually observed values of  $l_p(q_b)$  were used: since the latter do reflect some influence of the excluded volume effects implicitly, eq 33 is thus somewhat heuristic and phenomenological. Thus, it is interesting to compare our data as well to the original result of Birshtein et al.,<sup>26</sup> without adjusting any parameters. Their result is

$$q_{c}(q_{b}) = 2(4 + q_{b}^{-1})/\{2 + q_{b}^{-1} + [(2 + q_{b}^{-1})^{2} + 16]^{1/2}\}$$
(34)

While eq 34 clearly is inaccurate for  $q_b$  near  $q_b = 1$ , one sees that eq 34 becomes accurate as  $q_b \rightarrow 0$ , as expected from Figure 21a since the smaller  $q_b$  (and hence, the larger the persistence length, which scales as  $2l_p = 1 + 1/(2q_b)$  for  $q_b \rightarrow 0$ , see Figure 21b), the less important are the excluded volume effects in d = 3 dimensions (note that eq 34 is based on a treatment where immediate reversals were forbidden).

**4.4.** Parallel and Perpendicular Linear Dimensions of the "Pancake". In the adsorbed phase, the monomers of the chain are distributed in a disk-like volume with a radius  $(\langle R_{gl}^2 \rangle)^{1/2}$  and a height  $(\langle R_{gL}^2 \rangle)^{1/2} = \xi$  and so the average density  $\overline{\rho}$  of monomers in this disk is

$$\overline{\rho} = N/(\pi \langle R_{g\parallel}^{2} \rangle \xi) \propto l_{b}^{-3} N^{1-2\nu_{2}} (T_{c}/T-1)^{(3\nu-2\nu_{2})/\phi}$$
(35)

Note that this quantity behaves very differently for Gaussian chains, for which  $\nu_2 = \nu = 1/2$ ,  $\phi = 1/2$ , and chains subject to excluded volume interaction: for Gaussian chains we simply have  $\overline{\rho} \propto l_b^{-3}(T_c/T - 1)$ , i.e. there is no *N*-dependence, the density in the pancake is nonzero for  $N \to \infty$ , but in the excluded volume case we have

$$\overline{\rho} \propto l_b^{-3} N^{-1/2} (T_c/T - 1)^{0.55}$$
(36)

Since we have seen that the location of the adsorption transition is very accurately predicted by the mean field approach that neglects excluded volume, when the chains get rather stiff (Figure 21a), it is of interest to test the effect of stiffness on the average density, defined according to eq 35, as well. In addition, it is also of interest to consider the



**Figure 22.** Density  $\rho(z)$  plotted versus z for N = 25600,  $q_b = 0.02$  and several choices of  $q_b$  as indicated (a). Pancake thickness  $\langle z \rangle$  (b), rescaled average loop length  $\langle l_{loop} \rangle / \langle z \rangle$  (c), and rescaled height  $\xi / \langle z \rangle$  ( $\xi = \langle R_{g\perp}^2 \rangle^{1/2}$ ) (d) plotted versus  $T/T_c$  for N = 25600 and several choices of  $q_b$ , as indicated. In parts c and d, the corresponding data for several choices of  $q_b$  are presented by the same symbols as indicated in part b.



**Figure 23.** Log-log plots of  $\xi = (\langle R_{g\perp}^2 \rangle)^{1/2}$  (a),  $\langle R_{g\parallel}^2 \rangle^{1/2} / N^{3/4}$  (b), and  $\overline{\rho} = N/(\pi \langle R_{g\parallel}^2 \rangle \xi)$ , (c) versus  $T_c/T - 1$ . In part a, straight lines with exponents  $-\nu/\phi = -1$  (Gaussian chains) and  $-\nu/\phi \approx -1.22$  (SAW's) are included. In part b, straight lines with exponents  $(\nu_2 - \nu)/\phi = 0$  (Gaussian chains) and  $(\nu_2 - \nu)/\phi \approx 0.34$  (SAW's) are included. In part c, straight lines with exponents  $(3\nu - 2\nu_2)/\phi = 1$  (Gaussian chains) and  $(3\nu - 2\nu_2)/\phi \approx 0.55$  (SAW's) are included. Semilog plot of fraction of monomer surface contacts,  $N_s/N$ , versus  $T/T_c$  (d). Data are for chain length N = 25600 and several choices of  $q_b$  in part b are presented by the same symbols as indicated in part c.

distribution of the density within the "pancake": According to the mean field theory, this distribution in radial direction simply is the standard Gaussian distribution in d = 2 dimensions,

$$\rho(r) = N(\xi \pi \langle R_{g\parallel}^{2} \rangle)^{-1} \exp(-r^{2} / \langle R_{g\parallel}^{2} \rangle)$$
(37)

the scaling theory predicts a nontrivial power law for  $r \ll \langle R_{\rm ell}^{\ 2} \rangle^{1/2}$ , namely

$$\rho(r) \propto \xi^{-1} r^{1/\nu_2 - 2} \propto \xi^{-1} r^{-2/3}, \quad l_b \ll r \ll R_{g\parallel}^2$$
(38)

Note that  $\rho(r)$  is related to the Fourier transform of the (two-dimensional) structure factor.

In contrast, the distribution of the density  $\rho(z)$  in the *z*direction perpendicular to the adsorbing wall in the "pancake regime" quickly develops an exponential decay (Figure 22a). But  $\rho(z)$  is also useful since it yields an alternative definition of the pancake thickness, which we denote as  $\xi_{\rho}$ .

$$\xi_{\rho} = \sum_{z=1}^{\infty} \rho(z) z = \langle z \rangle \tag{39}$$

In Figure 22b a plot of  $\langle z \rangle$  versus  $T/T_c$  is shown, and parts c and d of Figure 22 plot the ratios  $\langle l_{\rm loop} \rangle / \langle z \rangle$  and  $\xi / \langle z \rangle$  versus  $T/T_c$ , for various choices of the parameter  $q_b$  that controls the chain stiffness. From Figure 22b, we conclude that increase of  $l_p$  at fixed ratio  $T/T_c$  does not cause a strong variation of  $\langle z \rangle$ , so an argument that increasing  $l_p$  (and hence the Kuhn length  $l_k = 2l_p$ ) just can be viewed as a trivial renormalization of all length scales by the same factor obviously cannot work for the adsorption problem. Note, in contrast, that both  $\langle l_{\rm loop} \rangle / \langle z \rangle$  and  $\xi / \langle z \rangle$  do increase significantly with increasing stiffness, however, and also  $\langle R_{g|l}^2 \rangle$  at fixed  $T/T_c$  increases strongly with  $l_p$ .

In Figure 23a, we present a log-log plot of  $\xi$  vs  $T_c/T - 1$  including data for a broad range of stiffness. Both straight lines with exponents  $-\nu/\phi = -1$  (appropriate for Gaussian chains) and  $-\nu/\phi = -0.588/0.483 \approx -1.22$  for SAW's are included. One sees that within our accuracy there is no strong effect of chain stiffness; the mean field exponents apply (if they apply at all) for data of rather stiff chains ( $q_b \leq 0.02$ ) rather close to  $T_c$ . Note that all these data apply to N = 25600 only, i.e. a chain length for which we know that in the bulk three-dimensional chains excluded volume effects still are rather weak, for stiff chains. As expected, the data do not scale perfectly with either choice of exponents, due to onset of slow crossover effects.

Figure 23b presents a plot of  $\langle R_{g\parallel}^2 \rangle^{1/2}/N^{\nu_2}$  vs  $T_c/T - 1$ . Figure 23c presents a plot of  $\overline{\rho}$  vs  $T_c/T - 1$  for the various stiffnesses, and Figure 23d presents the corresponding values of the adsorption order parameter  $N_s/N$ . All these data are compatible with a gradual crossover from a second-order transition, with nonmean field exponents, to a first-order adsorption transition, as  $q_b \to 0$  and hence  $l_p \to \infty$ . While we have found that  $\xi$  at fixed  $T/T_c$  exhibits almost no dependence on  $q_b$  and hence the persistence length of the chain, we see that  $\langle R_{g\parallel}^2 \rangle$ ,  $\overline{\rho}$  and  $N_s/N$  are strongly dependent on  $q_b$ . In the case of the density  $\overline{\rho}$ , this dependence on  $l_p$  just reflects the strong increase of  $\langle R_{g\parallel}^2 \rangle$  with  $l_p$  at fixed  $T/T_c$ . We get a rather clear evidence for the exponent 0.55 of eqs 35 and 36 for flexible chains, and possibly some indication for the exponent 1 (applying for Gaussian chains) for very stiff polymers.

#### 5. CONCLUDING REMARKS

In the present work, we have studied the effect of polymer stiffness on the adsorption of semiflexible polymers on flat structureless walls under good solvent conditions by large scale Monte Carlo simulations of self-avoiding walks (SAWs) on the simple cubic lattice, including an energy penalty  $\varepsilon_b$  for 90° kinks of the SAW on the lattice. In the three-dimensional bulk case our model calculation encompasses a variation of the persistence length  $l_{p}$ , which is extracted from the initial decay of the bond vector autocorrelation function, from about one lattice spacing (for fully flexible chains,  $\varepsilon_b = 0$ ) up to about 52 lattice spacings (for  $q_b = \exp(-\varepsilon_b/k_BT) = 0.005$ ). However, we find that  $l_p$  gets strongly renormalized by adsorption, i.e., we observe an enhancement of the actual persistence length by a factor up to a maximum value of about 2.3 (Figure 3). For intermediate adsorption strength, where still an appreciable fraction of bond vectors is contained in loops, we suggest that the effective stiffness is inhomogeneous along the chain; i.e., in large loops it should be close to its limiting three-dimensional

value, while in the trains (Figure 2) the persistence length should be close to the three-dimensional value.

The character of the adsorption transition is found to stay second order throughout, but it acquires more and more features of a first-order transition as  $q_b \rightarrow 0$  (and hence  $l_p \rightarrow \infty$ ). For large  $l_p$  we find that  $\varepsilon/k_{\rm B}T_c \propto 1/l_p$ , in agreement with the mean field theory of Birshtein et al.<sup>26</sup> and Khokhlov et al.<sup>29</sup> Applying the standard crossover scaling description that has been developed for flexible chains,<sup>4</sup> with and without excluded volume, we find that the data are compatible with the standard critical exponents ( $\nu \approx 0.588$ ,  $\nu_2 = 3/4$ ,  $\phi \approx 0.48$ ,  $\gamma_1^{sp}$  $\approx 1.22$ )<sup>14</sup> only for rather flexible chains, but not for rather stiff ones. In the three-dimensional bulk, it is known that increasing the persistence length causes the appearance of an intermediate regime of Gaussian behavior, consistent with the Kratky-Porod model, intruding in between the regime of rod-like behavior and SAW-like behavior.<sup>42,43</sup> Thus, one might expect that there exists a counterpart of this regime in the adsorption problem, too, where the (weakly adsorbed) chain can be pictured as a two-dimensional chain of blobs, such that inside a blob excluded volume effects are still negligible. However, little evidence for the existence of such a regime where Gaussian chain statistics rules the adsorption behavior has been found; rather we found that the crossover toward the first-order adsorption transition that appears (presumably) in the limit  $l_p\to\infty$  and is (presumably^{59}) characterized by a crossover exponent equivalent to the adsorption of an equivalent "renormalized" flexible chain (formed by a nonreversal random walk with bond length  $l_k = 2l_p$ .<sup>4</sup> It also differs from the adsorption of chains from a solution at the  $\Theta$  point.<sup>60</sup> For the two latter cases, clear evidence that the mean field exponents ( $\nu$ = 1/2,  $\phi = 1/2$ ,  $\gamma_1^{sp} = 1$ ) apply has been found,<sup>4,60</sup> unlike the present case. An interesting feature is that for strongly adsorbed semiflexible chains the average density in the "pancake" is orders of magnitude lower than for flexible polymers.

The fact that the critical line of adsorption transitions  $\varepsilon/k_{\rm B}T_{\rm c}$ = ln  $q_c(q_b)$  is rather accurately predicted by the mean field treatments that neglect excluded volume<sup>26,29</sup> should not be mistaken as the claim that these theories provide an accurate description of the properties of the adsorbed chain. It is wellknown<sup>42,43</sup> that in d = 2 dimensions there is no intermediate regime of Gaussian-like behavior in between rod-like and SAWlike behavior whatsoever. Thus, the lateral linear dimensions of the adsorbed coil scale like  $\langle R_{e\parallel}^2 \rangle \propto N^{3/2}$  rather than N, irrespective of chain stiffness, and as a consequence the average density  $\overline{\rho}$ ) of the "pancake" shows a scaling with  $1 - T/T_c$  and chain length N {eqs 35, 36} that differs strongly from mean field predictions (Figures 22 and 23). On the other hand, the behavior of the perpendicular linear dimensions  $(\langle z \rangle$  and  $\langle R_{a\perp}^2 \rangle^{1/2}$  and the loop length  $\langle l_{loop} \rangle$  is quite similar to the corresponding mean field results.<sup>26,29</sup> A particularly interesting finding is that a plot of  $\xi$  vs  $T_c/T - 1$  exhibits almost no dependence on the persistence length (Figure 23). In contrast, the parallel linear dimensions and the train length  $\langle l_{train} \rangle$ increases strongly with persistence length.

Finally, we emphasize that we did not see the least evidence for the multiple transitions (including a first-order transition from a weakly adsorbed pancake with small absolute value of the nematic order parameter to a strongly adsorbed pancake with pronounced nematic order) predicted by Kuznetsov and Sung.<sup>33–35</sup> However, they predict these transitions for a very wide range *b* of a square-well adsorption potential (V(z < b) = -U, V(z > b) = 0), with the transitions occurring for  $l_p/b < 1$ . Since their theory requires that the chains are very stiff,  $l_p \gg l_b$ , but one must also be able to study strongly adsorbed pancakes with linear dimensions  $\langle z \rangle$  in the range exceeding  $10l_p$  distinctly (see Figure 7 of ref 34, for instance), it is clear that they consider a parameter regime that is very different from the regime studied here (and by Birshtein et al.<sup>26,29</sup>). It is not clear to us whether their results are robust with respect to the assumption of a rather unphysical square-well adsorption potential (with a range  $b \gg l_p \gg l_b$ )

For very stiff chains, it is clear that our numerical data do not encompass the truly asymptotic regime: Figures 5c, 6c, 9c, and 10c clearly are caveats indicating that for  $I_p \ge 20$  chain lengths of the order  $10^4$  are still insufficient to pin down the asymptotic behavior. More efficient numerical methods will be required to go to chain lengths in the range  $10^6 \le N \le 10^7$ , and also a more detailed theoretical guidance for analysis of the various crossovers will be desirable. We hope that our study will stimulate such work, and will help already now for the understanding of the adsorption of semiflexible polymers on substrates such as double-stranded DNA.

Since our adsorption potential range equals the bond length  $l_b$ , it also is not possible to still have undulations of the chain conformation in *z*-direction (described by the Odijk<sup>61</sup> deflection length) within the range of the adsorption potential. Thus, the prediction that the adsorption threshold scales like<sup>62</sup>  $I_n^{-1/3}$  does not apply here.

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#### AUTHOR INFORMATION

#### Notes

The authors declare no competing financial interest.

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