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Monte Carlo Calculations of Polymer Adsorption at the Entrance of Cylindrical Pores in Flat Adsorbing Surfaces

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ABSTRACT

The influence of surface interactions on the conformation of flexible polymers partially confined inside narrow cylindrical pores in a flat surface is studied above the critical adsorption energy in a good solvent. We use a static configurational bias computational sampling method to calculate the adsorption free energy and the radius of gyration components parallel and perpendicular to the pore axis as a function of the polymer center of mass position at different degrees of confinement. We find strong free-energy minima just in front of the pore entry for all degrees of confinement studied. At the location of the free-energy minimum, polymers are partially adsorbed inside the pore and on the outer solid surface and adopt ‘‘drawing pin’’-like conformations. A distinct maximum in the average loop length at the pore entry indicates that the polymer bridges the pore entry of small pores.

Key Words: Polymer partitioning; Surface adsorption; Bond fluctuation model.

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INTRODUCTION

The conformation of a flexible polymer in solution depends on the nature of its environment. Changes in the solvent quality and polymer concentration, as well as spatial constraints imposed by confining geometries, affect the average coil shape and size to a large extent.\(^1\) In particular, the conformations of polymers and oligomers crossing the boundary between a bulk solvent and a porous medium deviate from those adopted in either of the two bulk phases. Despite the importance of this subject in, e.g., electrophoresis, chromatography, membrane ultrafiltration, and oligomer diffusion in zeolites, it has not been studied extensively,\(^2\) and many questions remain on phenomena occurring at the interface.

In previous work, we performed Monte Carlo computer simulations of flexible polymer chains at the entry of narrow cylindrical pores.\(^5\) At the interface, polymers, partially confined to pores smaller than the unperturbed (bulk) radius of gyration, assumed conformations not alike fully confined or unperturbed conformations. Instead, strongly asymmetric conformations with extended chain parts probing the pore entry were observed. When only excluded volume or weakly attractive interactions were present between polymer segments and the pore wall or the flat outer surface, the polymer was found to adopt an overextended conformation parallel to the pore axis, while penetrating the pore pre-dominantly with its terminal repeat units. This process causes the chain asphericity to run through a maximum when the chain center of mass has just entered the pore. When the chain center of mass diffuses further inside, the asphericity relaxes to a smaller value. These features, which may provide insight to the dynamic process of pore intrusion, all occur at the expense of the chain’s conformational entropy, while not being compensated for by a favorable energy of adsorption onto the pore wall. It is the purpose of this article to examine how the above picture changes when conditions of strong adsorption are simulated.

A significant number of computational studies on polymer partitioning in confined geometries are documented in the literature.\(^6\) Most studies dealt with polymer partitioning as a function of the degree of confinement and adsorption energy. Reports on cylindrical pores\(^7\) and slit-like pores\(^11,14\) showed that the partition coefficient in confinements increases with increasing adsorption potential and equals unity at the critical adsorption energy. Changes in polymer conformation as a function of the degree of confinement were reported for polymer chains between two flat walls\(^16\) The polymers changed from a three-dimensional coil to a two-dimensional pancake structure. Although polymer dynamics studies were carried out on polymer translocation through a small hole in an infinitely thin membrane,\(^17\) to the authors’ knowledge, the effects of chain adsorption on the intermediate conformations of polymers from a bulk solvent phase to a pore interior were not reported.

In this article, we examine the influence of surface adsorption on the conformations of partially confined polymers by means of computer simulation of a lattice chain model. We focus on chain conformation properties under conditions of strong adsorption, i.e., adsorption at conditions below the critical adsorption temperature, and on changes of the adsorption energy, entropy, and excess chemical potential (free energy) for various degrees of pore penetration. The calculation details are presented in the next section. We then present the results and summarize our conclusions.
SIMULATION DETAILS

The bond fluctuation lattice model\(^{[18]}\) was used together with a configurational bias sampling scheme\(^{[19]}\) to sample the chain conformation space. All simulated polymers are 50 monomers (M) long, each monomer occupying eight grid points (a box) on a three-dimensional simulation grid. All conformations are self-avoiding walks, and hence, monomer–monomer interactions are repulsive mimicking good solvent conditions. When one or more of the grid points of the monomer box is in contact with the wall, the monomer experiences an interaction energy \(\epsilon_{pw} = 0.0, 0.8, \text{ or } 1.2\) (units \(kT\)). This differs from our previous work, where the interaction energy was defined as the summed interaction energies of the four grid points in contact with the (flat) wall.\(^{[5]}\)

Because the bond fluctuation model allows for the configurational bias sampling algorithm to let each segment explore 108 directions, making it effectively an off-lattice case, the procedure is time consuming. For this reason, all conformations are generated by choosing each new monomer growth direction from a set of 50 directions randomly selected from the complete list of 108 possibilities. Configurational averages are obtained from the Rosenbluth average:\(^{[20]}\)

\[
\langle A \rangle_R = \frac{\sum_{n=1}^{N} W(n)A(n)}{\sum_{n=1}^{N} W(n)}
\]

in which \(A\) is the configurational quantity of interest, and \(W(n)\) denotes the Rosenbluth factor of chain conformation \(n\).

The chemical potential of a single chain as a function of its center of mass (CM) position along the \(z\)-coordinate is obtained from the chain Rosenbluth weight. In the configurational biased sampling algorithm, chains are inserted segment by segment. During the insertion of the \(i\)th segment, one has the choice of \(N\) possible directions and chooses the direction favoring the largest Boltzmann factor. The sum of Boltzmann factors of all possible directions during insertion of the \(i\)th segment is called the Rosenbluth factor \(w_i\):\(^{[20]}\)

\[
w_i = \frac{1}{N} \sum_{j=1}^{N} \exp(-\beta u_i(j))
\]

where \(\beta = 1/k_bT\), \(k_b\) is the Boltzmann constant; \(T\) is the temperature; and \(u_i(j)\) is the energy associated with inserting the \(i\)th segment in the \(j\)th direction. The chemical potential \(\mu\) of the inserted chain is calculated relative to the chemical potential of a nonreversing random walk, \(\mu_{id}\), in which monomer overlap is allowed. The reduced excess chemical potential \(\beta \mu_{ex} = \beta \mu - \beta \mu_{id}\) is calculated from the following:\(^{[21,22]}\)

\[
\beta \mu_{ex} = -\ln\left( \prod_{i=1}^{M} w_i \right) = -\ln(W)
\]

where \(M\) is the number of repeat units in the chain.
We calculated the excess chemical potential $\beta \Delta H_{ex}$ (relative to the chemical potential in the bulk solvent) as a function of the chain center of mass position along the pore axis, $CM(z)$. Chain conformations are generated from random positions in the available space between 100 grid points inside the pore ($z = -100$) and 100 grid points outside ($z = 100$). The interface is located at $z = 0$ (Fig. 1). Typically, 85 million conformations are generated, during which histograms $A(z_{CM}, n)$ and $W(z_{CM}, n)$ are updated ($z_{CM}$ is the chain center of mass $z$-position).

The simulation box is set up by putting a wall with a single straight pore along the $z$-direction in the middle of the box. The length of the cylindrical pore is large enough for the polymer to stretch out completely without finding both ends at opposite pore mouths. The dimensions of the simulation box are as follows: $L_{z,1} = L_{z,3} = 90$ grid points; $L_{z,2} = 201$; and $L_x = L_y = 82$ grid points (Fig. 1). The simulations are performed so as to obtain average chain conformational properties as a function of the chain center of mass $z$-coordinate, $CM(z)$. Periodic boundary conditions are applied in all three directions. The conformations located at $z = 100$ do not experience the wall and resemble unconfined polymers in a good solvent at infinite dilution. The conformations located at $z = -100$ are fully confined by the pore geometry. The pore radius $R_p$ is varied such that the coil-to-pore size ratio $\lambda$, defined as $\lambda = R_g / R_p$, varies between $\lambda = 3.0$ and $\lambda = 0.5$. The polymer radius of gyration, $R_g$, under athermal conditions equals 11.3.

For $z > 0$, the $x$ and $y$ position coordinates of the first monomer of each newly generated chain are chosen within a radius of $2.5 R_g$ around the pore axis. For all $\lambda$-values studied in this work, this radius exceeds $R_p$. Only fully grown chains with centers of mass within a radius $R_p$ from the axis are considered in the statistical sampling of conformational averages. As a consequence, porosity (pore concentration) effects are absent in excess chemical potentials and chain conformational properties near the pore entrance. This choice is motivated by two reasons. First, we want to understand conformational properties of chains that partially entered a pore, while their remaining unconfined monomers should still have the opportunity to adsorb onto the outer surface facing the bulk solution. Thus, conformations of adsorbing chains not experiencing the pore must not be considered. Second, we hope to obtain some insight to the chain conformational free energy along a coordinate perpendicular to an adsorbing surface with one cylindrical pore in the center. This chemical potential (as

![Figure 1.](image.png)
well as its energetic and entropic components, discussed later) may contain information on energetic or entropic barriers at the pore entry and, thus, should exclude contributions of adsorbed chains not experiencing this entry.

The center of mass of incomplete chains resulting from failed growth attempts (where a term \( W = 0 \) is contributing to the average Rosenbluth factor) was calculated using only the successfully grown monomers in the chain. Tests in small confinements, typically at \( \lambda = 1.6 \), and a monomer–wall interaction of \( \epsilon_{pw} = 1.2 \ kT \) resulted in an acceptance ratio of 99.89% inside the pore. In the rare case of a premature growth termination, 65% of those chains terminated at the 30th monomer or at higher monomer indices. Almost all growth attempts in the bulk solvent phase are successful.

**RESULTS**

**Critical Adsorption Energy**

To identify the regimes of weak and strong adsorption, we calculated the critical adsorption energy, \( \epsilon_{cr} \), using the method of Gong and Wang.\(^{15}\) The method involves the calculation of the chemical potential \( \beta \Delta \mu_{ex} \) of adsorbed chains relative to the value in the bulk solvent as a function of the monomer–wall adsorption energy, \( \epsilon_{pw} \), and the polymer chain length. The value of \( \epsilon_{pw} \), where the chemical potentials for different chain lengths coincide, corresponds to the critical adsorption energy. This assignment is based on the argument that below the adsorption transition (small \( \epsilon_{pw} \)), longer chains are more strongly repelled by the surface than shorter chains; whereas beyond the adsorption transition, longer chains are more strongly attracted by the surface than shorter chains. At the critical adsorption point, the entropic repulsion is balanced by the energetic attraction and becomes independent of the chain length.\(^{23}\) Although Gong and Wang used conformations terminally anchored to the surface to determine \( \epsilon_{cr} \), we used no such constraint and sampled polymer conformations above a flat surface, taking those into account only for calculating \( \beta \Delta \mu_{ex} \), if at least one of their repeat units is in contact with the surface. We used polymer chain lengths of 30, 50, 70, and 100 repeat units. Fig. 2 shows \( \beta \Delta \mu_{ex} \) as a function of \( \epsilon_{pw} \) for the various chain lengths. The critical adsorption point is located at \( \epsilon_{cr} = 0.96 \ kT \). We note that theoretically, one expects \( \beta \Delta \mu_{cr} = 0 \). We find \( \beta \Delta \mu_{cr} = -0.40 \), which compares to \( \beta \Delta \mu_{cr} = -0.346 \) reported by Gong and Wang.\(^{15}\)

**Excess Chemical Potential, Interaction Energy, and Entropy Profiles**

At \( \epsilon_{pw} = 0.0 \ kT \), changes in the chain’s excess chemical potential are due solely to entropic effects. The change in the excess chemical potential for various pore sizes as a function of the center of mass position is shown in Fig. 3(A), as already found in previous work.\(^{5}\) Negative center of mass \( [CM(z)] \) values indicate that the polymer center of mass is located inside the pore.

Following the polymer center of mass from the bulk solvent toward the pore, the excess chemical potential \( \beta \Delta \mu_{ex} \) increases due to loss of conformational entropy when the center of mass is located in the vicinity of the interface. It increases further until its
center of mass is far inside the pore. The plateau value of $\beta \Delta \mu_{ex}$ inside the pore is reached at $CM(z)$-positions further inside, when $\lambda$ is larger. For $\lambda > 1$, $\beta \Delta \mu_{ex}$ does not increase as steeply inside the pore as outside the pore, due to the asymmetric conformations present at the interface: the part of the polymer inside the pore is stretched, but the part outside the pore remains a coil-like conformation.[5,24,25] The introduction of weakly attractive interactions ($\epsilon_{pw} < \epsilon_{cr}$) of the monomers with the wall does not change this picture other than reducing the steep increase of $\beta \Delta \mu_{ex}$ by partly compensating the entropy cost with an energetic payback resulting in increasing partition coefficients.[5]

This picture changes completely when using monomer–wall interactions $\epsilon_{pw}$ above the critical adsorption energy $\epsilon_{cr}$. The excess chemical potential profiles for several $\lambda$ values as a function of the polymer $CM(z)$ at $\epsilon_{pw} = 1.2 \, kT$ ($\epsilon_{cr} = 0.96 \, kT$) are shown in Fig. 3(B). The most striking difference from the profiles in Fig. 3(A) is the minimum just in front of the interface. Chains apparently prefer the interface over the bulk solvent phase and the pore interior. A similar kind of observation was made for the partitioning of liquid hexadecane molecules at the interface between the zeolite silicalite and liquid hexadecane.[2] The depth of the minimum is about $3.5 \, kT$ relative to the solvent bulk value for all the $\lambda$ values, except for wide pores ($\lambda = 0.5$), where the minimum equals $2 \, kT$. The smaller excess chemical potential drop for $\lambda = 0.5$ is caused by the large pore cross-sectional area that inhibits chain repeat units from having favorable energetic contacts with the flat surface facing the bulk solvent phase. It also explains why the excess chemical potential inside the pore is less negative for $\lambda = 0.5$ than for $\lambda = 1.0$, also reported by Cifra and Bleha for this range of confinement degrees.[14]

As already stated, the excess chemical potential profile at weakly attractive segment–wall energies ($\epsilon_{pw} < \epsilon_{cr}$) does not differ in shape from the situation in which the
segment–wall interaction is repulsive (Fig. 3(A)). When the excess chemical potential as a function of the center of mass position is decomposed into the energetic and entropic contributions, as done in Fig. 4 for $\epsilon_{pw} = 0.8\ kT$ and $\lambda = 1.6$, one can see that at as far as 30 grid points (about three bulk radii of gyration) away from the interface, the energy already decreases. Extended conformations must therefore occur, which

**Figure 3.** Excess chemical potential profiles versus the chain center of mass position along the pore axis, $CM(z)$, at $\epsilon_{pw} = 0.0\ kT$ (A) and at $\epsilon_{pw} = 1.2\ kT$ (B) for various $\lambda$-values. Positive $CM(z)$ positions denote the bulk solvent region; negative values denote the pore region.
have some of their monomers adsorbed. Interestingly, this energy is compensated for by a reduction of the conformational entropy, which causes this adsorption phenomenon to be nonvisible in $bD_{\text{m}}^{\text{ex}}$. The excess chemical potential starts to deviate from the bulk solvent value at much smaller distances (about one radius of gyration) from the interface, where the dominant entropic contribution causes $bD_{\text{m}}^{\text{ex}}$ to rise. The entropy keeps decreasing faster than the adsorption energy, causing the excess chemical potential to rise gradually toward its constant value inside the pore. At 20 grid points (approximately $2R_g$ inside the pore), all three quantities reach a constant value.

Shown in Figs. 5(A), B, and C are the entropic and energetic contributions to the excess chemical potential profiles at $\epsilon_{\text{pw}} = 1.2kT$ for $\lambda = 2.1, 1.6$, and 0.5, respectively. Again, we note that at about two to three bulk radii of gyration away from the interface, the energy and entropy changes compensate in the chemical potential. The minimum in $b\Delta\mu_{\text{ex}}$ at the pore entry cannot be attributed to an extremum in the energetic or entropic component. Rather, it occurs because, upon approaching the pore entry from the bulk solvent, the adsorption energy drops faster than the entropy, while the reverse applies when the polymer enters the pore. For $\lambda = 0.5$ and 1.6 at full confinement ($z < -20$), the adsorption energy outweighs the conformation entropy loss, causing partition coefficients $K = e^{-b\Delta\mu_{\text{ex}}} > 1$.

For $\lambda = 2.1$ (Fig. 5(A)), the entropy loss upon entering the pore is much stronger than the adsorption energy gain, causing the curves of $bE_{\text{ex}}$ and $\Delta S_{\text{ex}}/k$ to intersect at approximately $CM(z) = -12$. This causes a positive value of $b\Delta\mu_{\text{ex}}$ and, consequently, a partition coefficient smaller than unity. Large degrees of confinement result in a greater loss of conformational entropy, whereas the number of adsorbed monomers, the adsorption energy, is limited by the number of monomers in the chain. It is therefore
not surprising that at a certain degree of confinement, the entropy will dominate over the adsorption energy. In this system (chain length $M = 50$), at $\epsilon_{pw} = 1.2 \text{ kT}$, this happens for values of $\lambda$ somewhere between 1.6 and 2.1. This “critical degree of confinement” depends on the chain length and will be larger for stronger attractive monomer–wall potentials. Although Cifra and Bleha concluded that the partition

Figure 5. Excess chemical potential (left scale), energy and entropy (right scale), as a function of the polymer center of mass (CM) for (A) $\lambda = 2.1$, (B) 1.6, and (C) 0.5 at $\epsilon_{pw} = 1.2 \text{ kT}$.
coefficient rises with increasing degrees of confinement above the critical adsorption energy, they did not report data for confinement degrees larger than 1.6.\(^{[14]}\)

In Fig. 5(C), the same quantities for \(\lambda = 0.5\) are shown. Although the entropy, \(\Delta S_{ex}/k\), inside the pore is much higher compared to the smaller pores, i.e., \(-12.0\) instead of \(-22.5\) for \(\lambda = 1.6\), the adsorption energy, \(\beta \Delta E_{ex}\), has a less negative value \((-13.0\) instead of \(-23.5\) for \(\lambda = 1.6\)), because fewer monomers are near the pore wall to experience favorable monomer–wall contacts. Like for \(\lambda > 0.5\) at \(z > 0\), in the vicinity of the interface, the value of \(\beta \Delta \mu_{ex}\) decreases due to a faster drop of the adsorption energy compared to the entropy. However, inside the pore, the entropy loss is, to a much larger extent, compensated for by a favorable energy, causing the excess chemical potential barrier for entering the pore to get much smaller in comparison to the smaller pores (Figs. 5(A) and B).

To illustrate how the excess chemical potential minimum develops just in front of the pore entry, presented in Fig. 6 is \(\beta \Delta \mu_{ex}\) versus the center of mass position at a degree of confinement \(\lambda = 1.6\) for various \(\epsilon_{pw}\) values. As can be seen in Fig. 6, an increasing \(\epsilon_{pw}\) reduces \(\beta \Delta \mu_{ex}\) inside the pore. Upon approaching the critical adsorption energy \(\epsilon_{cr}\) (\(\epsilon_{pw} = 0.96\ kT\)), the excess chemical potential profile starts to form a shallow minimum at 10 grid points (approximately one bulk radius of gyration) away from the interface. A minimum located at four grid points away from the interface can eventually be found at \(\epsilon_{pw} = 1.0\ kT\), and it moves closer to the interface for \(\epsilon_{pw} = 1.2\ kT\), where the minimum becomes strong.

We end this section by noting that at \(\lambda\)-values larger than 2.1, artefacts related to the underlying lattice appear in the excess chemical potential. Because all geometries including the cylindrical pore are modeled on a lattice, a scatter on the number of available adsorption sites as a function of the pore radius appears for \(\lambda > 2.1\) due to
irregularities of the cylinder. This causes artefacts in the energy inside the cylindrical pore. Conclusions for $\lambda$ values greater than 2.1 should, therefore, be taken with caution.

Conformational Changes

The conformational properties of chains adsorbed above the critical adsorption point, $\epsilon_{cr}$, are expected to deviate strongly from those observed below $\epsilon_{cr}$. In previous work, we used the chain asphericity to characterize the three-dimensional conformation of nonadsorbing polymers.\[5\] The asphericity replaced the radius of gyration components (parallel and perpendicular to the pore axis) with a single quantity. Here, we expect to see many conformational changes depending on the polymer position relative to the surface. The polymer radii of gyration components perpendicular and parallel to the pore axis provide greater detail of such conformational changes and are examined here. The $R_g$ components are calculated as follows:

\begin{equation}
\langle R^2_{g,\text{parallel}} \rangle = \frac{1}{M} \sum_{i=1}^{M} \left( r_{z,i} - r_{z}^\text{cm} \right)^2
\end{equation}

\begin{equation}
\langle R^2_{g,\text{perpendicular}} \rangle = \frac{1}{M} \sum_{i=1}^{M} \left( \frac{(r_{x,i} - r_{x}^\text{cm})^2 + (r_{y,i} - r_{y}^\text{cm})^2}{2} \right)
\end{equation}

where $M$ is the number of repeat units.
Shown in Fig. 7(A) are $R_g^2$ parallel and $R_g^2$ perpendicular as functions of the polymer center of mass position for $\lambda = 1.6$ at $\epsilon_{pw} = 0$ $kT$ (repulsive walls) and at (B) $\epsilon_{pw} = 0.8$ $kT$ (weakly attractive walls) for $\lambda = 1.6$.

Shown in Fig. 7(A) are $(R_g^2)_{\text{parallel}}$ and $(R_g^2)_{\text{perpendicular}}$ as functions of the polymer center of mass position for $\lambda = 1.6$ at $\epsilon_{pw} = 0$ $kT$. Approximately 24 grid points (2.5 bulk radii of gyration) away from the surface, the parallel component starts to decrease from its bulk solvent value of 43, while the perpendicular component increases slightly due to the repulsive nature of the interface. At a chain center of mass position of eight...
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grid points in front of the interface, the parallel component increases steeply. At this distance, most monomers remain outside the pore, but a few poke inside, giving rise to a sudden increase of $\langle R_g^2 \rangle$ at $z = -12$, after which the parallel “overextension” disappears, and $\langle R_g^2 \rangle$ assumes a value of approximately 100. At the same time, $\langle R_g^{\perp} \rangle$ reaches a value of 7.

Similar phenomena can be observed under conditions of weakly attractive interactions. For $\epsilon_{pw} = 0.8 \ kT$, the $R_g$ component perpendicular to the pore axis increases slightly until it is six grid points in front of the surface. After that, it gradually decreases toward a lower constant value approached at 21 grid points inside the pore (Fig. 7(B)). The parallel component starts to decrease at 15 grid points away from the interface, toward a minimum at four grid points in front of the interface. The weak monomer–wall interactions cause a somewhat weaker chain deformation compared to what happens close to repulsive walls (Fig. 7(A)) under identical degrees of confinement.\[5\]

The situation above the critical adsorption energy changes dramatically, as shown in Fig. 8 for $\epsilon_{pw} = 1.2 \ kT$. Here, two clear maxima for $\langle R_g^{\perp} \rangle$ inside the pore and outside the pore, as well as a maximum in $\langle R_g^{\perp} \rangle$ on the interface, attract the attention. These peaks and valleys will be explained based on the snapshots shown in Fig. 9. Following the polymer center of mass from the bulk solvent toward the pore in Fig. 8, the $\langle R_g^{\perp} \rangle$ increases from its bulk solvent value of 43, starting at approximately 25 grid points away from the interface, until it reaches a maximum of 61 at 14 grid points in front of the interface (Situation I). The $\langle R_g^{\perp} \rangle$ has a shallow minimum of 41 at that point. This corresponds to polymer chains stretching to the surface to come into contact with the wall to experience the favorable monomer–wall interactions (see Fig. 9, Situation I). As can be seen in Fig. 5(B), this leads to a reduction of

![Figure 8](image-url)  

**Figure 8.** Radius of gyration components as a function of the center of mass (CM) position at $\epsilon_{pw} = 1.2 \ kT$ (strongly attractive walls) and $\lambda = 1.6$. 
the conformational entropy, however, the energy gain is sufficiently large to lower the conformational excess chemical potential relative to the value in bulk solution.

At positions closer to the interface, the $R^2_{g, parallel}$ has a clear minimum just before the interface of only 14, and the $R^2_{g, perpendicular}$ has a strong maximum of 59 (Situation II). In this situation, chains preferentially adsorb on the flat surface facing the bulk solution, while a small part of the repeat units in front of the pore tends to adsorb onto the inner pore surface. Chain parts adsorbed on the surface outside the pore can expand in the $x$ and $y$ directions in order to maximize the surface coverage, causing the perpendicular part of $R_g$ to increase and the parallel part to become smaller. The dominant polymer conformations found in Situation II are typically partly adsorbed inside the pore and on the outer surface in “hooked” structures or resemble “drawing-pins” (Fig. 9, Situation II). Also, conformations adsorbed on the outer surface encircling and bridging the pore entry, not penetrating the pore, are found in abundance. Note that at the $CM(z)$ position corresponding to Situation II, the minimum in the excess chemical potential (Fig. 5(B)) occurs. These conformations, therefore, dominate the polymer partitioning at infinite dilution.

At 12 grid points inside the pore, there is a small maximum in $R^2_{g, parallel}$ of 102, similar to the maximum at $\epsilon_{pw} = 0 \ kT$, and also caused by part of the polymer chain being stretched inside the pore and part still residing outside the pore but now adsorbed on the outer surface. Because of the adsorption features shown in Fig. 9, the polymer is no longer as stretched in the direction parallel to the pore axis in comparison to its complete confined conformation, which starts at approximately 25 grid points inside the pore (Situation III). The maximum in $R^2_{g, parallel}$ is about 20 units higher compared to $R^2_{g, parallel}$ at $z = -25$, in contrast with a difference of approximately 35 $R_g^2$ units in the case of $\epsilon_{pw} = 0 \ kT$.

Smaller degrees of confinement, e.g., $\lambda = 0.5$, also show these distinct maxima and minima. The maximum inside the pore for the parallel component of $R_g^2$, however, is almost vanished, and the maximum in $R^2_{g, parallel}$ in front of the interface is somewhat smaller and becomes even smaller for smaller degrees of confinement (not shown).

### Loops and Trains

Data on loops and trains at interaction energies above the critical adsorption energy give valuable information about conformations of adsorbed polymers in the interface

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**Figure 9.** Snapshots of partially confined polymers at various degrees of penetration at $\epsilon_{pw} = 1.2 \ kT$ and $\lambda = 1.6$. The number corresponds to those shown in Figure 8.
region. In Fig. 10(A), the loop and train length of adsorbed polymers is plotted as a function of the center of mass position for $\lambda = 1.6$ and $\epsilon_{pw} = 1.2 \, kT$. The numbers of loops and trains in the same situation are shown in Fig. 10(B).

In Fig. 10(A), the first thing that attracts attention is the maximum in the loop length ($\lambda = 1.6$) approximately four grid points away from the interface. The train

![Figure 10. Loop and train lengths (A) and amount of loops and trains (B) of adsorbed polymers versus the chain center of mass position at $\epsilon_{pw} = 1.2 \, kT$ and $\lambda = 1.6$.](image-url)
length does not show such a maximum and increases gradually toward a constant value inside the pore. The peak in the loop length in front of the interface vanishes for $\lambda = 0.5$ and is replaced by a sharp kink to a plateau value at $CM(z)$ values of 0 and lower. The maximum in loop length at $\lambda = 1.6$ indicates that parts of the polymer chain at the interface bridge the pore entry. Bridging of the pore entry becomes less probable for increasing pore sizes.

Shown in Fig. 10(B) is a gradual increase in the number of trains and loops with decreasing center of mass positions. At full confinement, the numbers of loops and trains reach values slightly larger than 7 and 8, respectively. The train length (Fig. 10(A)) is already constant at the interface. The trains start to appear at 30 grid points away from the interface, while the loops appear at approximately 25 grid points away. After that, the number of loops $n_{\text{loop}}$ equals $n_{\text{train}} - 1$. Larger degrees of confinement show similar effects.

**CONCLUSIONS**

Configurational bias Monte Carlo simulations with the bond fluctuation model were performed to study the adsorption free energy and conformational properties of flexible polymers near the entrance of cylindrical pores in a flat surface and at various degrees of pore penetration. The system studied in this work consists of a flat, adsorbing surface containing a pore of variable dimensions $0.5 \leq \lambda (= R_g/R_{\text{pore}}) \leq 3$ in contact with a good solvent containing a polymer with chain length $N = 50$ at infinite dilution.

Upon approaching the adsorption transition, excess chemical potential profiles computed as a function of the chain center of mass position along the pore axis develop a minimum just in front of the pore entry at the bulk solvent side of the interface for all pore sizes examined in this work. The polymer favors this location near the interface over the bulk solution, where its conformational entropy is at a maximum, and the pore interior, where its adsorption energy is at a minimum. The chain conformation at this point is best characterized as a “drawing-pin,” which has most of its repeat units adsorbed on the outer surface and some on the inner pore surface. Train lengths examined as a function of the chain center of mass position reveal no differences between adsorption onto the inner pore surface and the flat outer surface. The loop length as a function of the chain center of mass position for small pore sizes ($\lambda = 1.6$) runs through a maximum just outside the pore, indicating that the chain bridges the pore entry.

Above the critical adsorption transition, the excess chemical potential profiles start to decrease upon approaching the surface from the bulk solution at center of mass distances approximately two bulk radii of gyration away from the surface. At this distance, the radius of gyration component parallel to the pore axis increases considerably, due to the attempt of the chain to bring as many as possible of its repeat units into contact with the surface. At distances smaller than one bulk radius of gyration away from the surface, the parallel $R_g$ component decreases, while the perpendicular component increases as a consequence of the formation of “drawing-pin”-like conformations.
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