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Semiflexible Macromolecules with Discrete Bond Angles Confined in Nanoslits: A Monte Carlo Test of Scaling Concepts

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ABSTRACT: Single semiflexible polymer chains confined in a planar slit geometry between parallel nonadsorbing repulsive walls a distance D apart are studied by Monte Carlo simulations of a lattice model, for the case of good solvent conditions. The polymers are modeled as self-avoiding walks on the simple cubic lattice, where every 90° kink requires a bending energy ε_b . For small $q_b = \exp(-\varepsilon_b/k_{\rm B}T)$ the model has a large persistence length I_p



(given by $l_p \approx 1/(4q_b)$ in the bulk three-dimensional dilute solution, in units of the lattice spacing). Unlike the popular Kratky– Porod model of worm-like chains, this model takes both excluded volume into account and approximates the fact that bond angles between subsequent carbon–carbon bonds of real chains are (almost) restricted to large nonzero values, and the persistence length is controlled by torsional potentials. So the typical local conformation in the model is a straight sequence of (on average) l_p bonds (roughly corresponding e.g. to an all-trans sequence of an alkane chain) followed by a 90° kink. While under weak confinement ($D \gg l_p$) the model (for very long chains) still is compatible with the Daoud–de Gennes scaling theory, for strong confinement ($D \le l_p$) strong deviations from the predictions based on the Kratky–Porod model are found.

1. INTRODUCTION AND OVERVIEW

Semiflexible polymers confined into nanoscopic channels have found much recent interest, both from analytical theory¹⁻¹⁹ and simulation²⁰⁻²³ as well as from experiment.²⁴⁻³¹ If the distance D between the confining walls of the planar slit channel is much larger than the persistence length l_p of the semiflexible macromolecule, and one considers good solvent conditions, the problem is essentially equivalent to the classical problem of confined flexible polymers considered by Daoud and de Gennes.³² These authors considered completely flexible chains where N bonds of length l_p are linked together, respecting excluded volume. A free chain then has linear dimensions of order $R_{\rm free} \approx l_b N^{\nu}$, with ³³ $\nu \approx 0.588$ (here and in the following, prefactors of order unity will be ignored). When R_{free} and D are of the same order, a crossover to a quasitwo-dimensional self-avoiding walk occurs, which is charac-terized by the exponent³⁴ $\nu_2 = 3/4$. The chain can be pictured as a two-dimensional self-avoiding walk of "blobs"32,34 of diameter D. Each blob satisfies three-dimensional self-avoiding walk statistics, and hence $D \approx l_{\mu}g^{\nu}$, with g monomers per blob, and altogether there are $n_{blob} = N/g$ blobs. Hence, the linear dimension of a chain in the directions parallel to the confining walls is $\{n_{blob} = N(l_b/D)^{1/\nu}\}$

$$R_{\parallel} = Dn_{\rm blob}^{3/4} = l_b N^{3/4} (D/l_b)^{1-3/(4\nu)} \approx l_b N^{3/4} (D/l_b)^{-1/4}$$
(1)

where in the last step the Flory approximation $\nu \approx 3/5^{32,34,35}$ was used. According to the blob picture, the free energy cost per blob is the thermal energy $k_{\rm B}T$, and hence the free energy cost of confinement is

$$\Delta F/k_{\rm B}T = n_{\rm blob} = N(l_b/D)^{1/\nu} \approx N(l_b/D)^{5/3}$$
(2)

Thus, the force $\mathcal{F}(D) = -\partial(\Delta F)/\partial D$ acting on the walls scales like $\mathcal{F}(D) \propto ND^{-8/3}$.

However, the generalization of this approach to semiflexible polymers is somewhat subtle. If an increase of the persistence length l_n is effected by an increase of effective chain "thickness" (this is the case for "bottle brush" polymers^{36–39} where it was found that $l_p \approx 3R_{cs}$, where R_{cs} is the cross-sectional radius of the cylindrical brush^{40,41}), all lengths simply have to be rescaled by replacing *N* by $N' = Nl_b/l_p$ and l_b by l_p in eqs 1 and 2. This case shall be out of consideration here, where we assume that the chain thickness (and hence the strength of excluded volume, as measured e.g. by the second virial coefficient $v_2^{34,35}$) stays constant. For example, for alkane chains one can vary l_p by changing the temperature.^{35,42} Then the effect of the excluded volume interactions becomes less and less important, the larger l_{p} becomes, and as consequence the conformation of a coil in the bulk (in dilute solution) is characterized by three regimes.^{39–41,43–47} The radius *R* of the coil can then be written as

$$R \approx L \equiv Nl_{b}, \quad L < l_{p} \text{ (rod-like chain)}$$
(3)

$$R \approx (l_p L)^{1/2}, \quad l_p < L < l_p^3/l_b^2$$
 (Gaussian chain) (4)

$$R \approx (l_p l_b)^{1/5} L^{3/5}, \quad L > l_p^{-3} / l_b^{-2} \text{ (swollen, SAW-like chain)}$$
(5)

Thus, when the contour length L of a stiff polymer increases, there are three distinct power laws for the end-to-end distance R_e (or the gyration radius R_e , which differs from R_e only by a

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Figure 1. Schematic log–log plot of the chain linear dimensions R_{\parallel} , R_{\perp} of a confined semiflexible polymer with contour length L and persistence length I_p as functions of the reduced contour length L/I_b (I_b is the bond length). Part (a) shows the case of $I_p < D < R^*$, part (b) the case $R^* < D$, with $R^* \approx I_p^{-2}/I_b$ describing the size of a free chain where excluded volume starts to dominate. The chain linear dimensions R_{\parallel} , R_{\perp} parallel and perpendicular to the confining walls are essentially the same and equal to the radius R of a free, unconfined chain, as long as R < D, while for R > D we have $R_{\perp} = D$, while R_{\parallel} continues to increase with increasing L/I_b . For $L/I_b < I_p/I_b$ the chains behave like rigid rods, while for $L/I_b > I_p/I_b \gg 1$ a regime of Gaussian statistics of distances in the chain occurs. If $D < R^*$, one finds a crossover at $L = L_c = D^2/I_p$, where R_{\perp} saturates at $R_{\perp} = D$, while R_{\parallel} increases further with L up to $L = L^*$ (corresponding to $R_{\parallel} = R^*$), where one has compressed Gaussian coils (the force of the walls scales as $\mathcal{F} \propto LI_p/D^3$ in this regime). For still longer chains ($L > L^*$) in this regime of moderately weak compression a crossover to $R_{\parallel} = R_{\perp}$ increase with $L^{3/5}$ like a free chain. Note that for flexible chains where I_p and I_b are of the same order, both the rod regime and the Gaussian regime disappear from the picture, and instead of three crossovers a single crossover remains. Finally, we emphasize that all crossovers are smooth, there are no kink singularities at the log–log plot, but a gradual change of the slope spread out over typically a full decade of L/I_b occurs.

numerical factor) as a function of *L*. But since the crossovers between the three regimes are smooth and extend typically over 1 decade in *L* each, $^{39-41,46,47}$ one needs to vary *L* over a wide range to see these crossovers, and hence experimentally only few data exist (e.g., ref 48) which exhibit this behavior clearly.

Note that the crossover contour length $L^* = l_p^3/l_b^2$ corresponds to a crossover radius of the coil R^*

$$R^* \approx l_p^{-2} / l_b \tag{6}$$

This quantity is central for a discussion of confinement effects: when $l_p < D < R^*$ and $L < L^*$, we simply encounter the problem of confining a Gaussian chain. Since for Gaussian chains the different Cartesian coordinate components of the distance vectors are uncoupled, we simply can conclude that the parallel and perpendicular components of the radii scale as^{49,50} for $L > L_c = D^2/l_p$

$$R_{\perp} \approx D, \quad R_{\parallel} \approx (l_p L)^{1/2}, \quad l_p < D < R^* \text{ and } L < L^*$$
(7)

and the free energy excess (due to compression of a Gaussian chain from a linear dimension $(l_p L)^{1/2}$ to *D* in the *z*-direction) is^{49,50}

$$\Delta F/k_{\rm B}T \approx (Ll_p)/D^2 \tag{8}$$

and hence the force scales as $\mathcal{F} \propto Ll_p/D^3$.

We next consider the case that we still have $I_p < D < R^*$ but $L > L^*$. Noting that eq 5 can simply be rewritten as $R = (L/L^*)^{3/5}R^*$, we see that the obvious interpretation of eq 5 is that a long chain in dilute solution can be viewed as a self-avoiding string containing $n_{\text{blob}} = L/L^*$ blobs of radius R^* , while inside a

blob we have Gaussian statistics. The obvious generalization to the confined case then is (cf. eq 1) a string of elliptic blobs (linear dimension D in z-directions, R^* in parallel directions)

$$R_{\parallel} = R^* n_{\text{blob}}^{3/4} = R^* \left(\frac{L}{L^*}\right)^{3/4} = (l_p^2/l_b) L^{3/4} l_b^{3/2} l_p^{-9/4}$$
$$= l_b^{1/2} l_p^{-1/4} L^{3/4}$$
(9)

and the free energy cost is written as product of the number of blobs times the free energy cost of compressing a Gaussian blob:

$$\Delta F/k_{\rm B}T \approx (Ll_p)n_{\rm blob}/D^2 \approx (L/D)^2 (l_b/l_p)^2 \tag{10}$$

The surprising conclusion of eqs 9 and 10 is that there exists a regime where for fixed *D* and fixed *L* both R_{\parallel} and ΔF decrease when l_p is increased: this is due to the fact that the regime where Gaussian statistics applies becomes more extended (of course, this is an intermediate regime only, since one still must respect $l_p < D$ as well).

Another regime occurs when $D > R^*$ but $L > L^*$. Equating R and D yields another crossover contour length L'_c

$$L'_{c} = \left[D/(l_{b}l_{p})^{1/5}\right]^{5/3} = D^{5/3}(l_{b}l_{p})^{-1/3}$$
(11)

and then we expect that the chain is described as a twodimensional self-avoiding walk of $n_{blob} = L/L'_c$ blobs

$$R_{\parallel} = Dn_{\rm blob}^{3/4} = DL^{3/4} D^{-5/4} (l_b l_p)^{+1/4} = L^{3/4} D^{-1/4} (l_b l_p)^{1/4}$$
(12)

Equation 12 has previously been proposed by Cifra²² using a Flory argument.^{34,35,50} However, it is well-known (see e.g. ref 51) that the Flory free energy minimization procedure can yield

correct chain linear dimensions, due to a cancellation of errors, but yields wrong estimates for the free energy itself. So the free energy cost of confinement can not be obtained from the Flory treatment, and we solely have to rely on the blob argument to conclude that

$$\Delta F/k_{\rm B}T \approx n_{\rm blob} = (L/L'_{c}) = LD^{-5/3} (l_{b}I_{p})^{1/3}$$
$$= ND^{-5/3} (l_{b}^{4}I_{p})^{1/3}$$
(13)

Note that in this regime there is a weak enhancement of both R_{\parallel} (by a factor $(l_p/l_b)^{1/4}$) and ΔF (by a factor $(l_p/l_b)^{1/3}$) relative to the result for a flexible chain, when we compare eqs 12 and 1 or eqs 13 and 2, respectively. We also note that Cifra²² did not discuss the other regimes (considered in eqs 7–10. Figure 1 gives a graphical representation of the predicted crossovers.

Of course, the most interesting case (relevant experimentally for confinement of very stiff biomolecules, such as doublestranded DNA or even actin) is the case $D < l_p$. Considering not too long chains, for which hairpin formation can be neglected, excluded volume effects for confined stiff chains are considered to be unimportant. Then the standard description that is postulated for semiflexible chains is the Kratky–Porod model⁵²

$$\mathcal{H}_{\rm KP}(\vec{r}(s)) = \frac{\kappa}{2} \int_0^L \mathrm{d}s \left(\frac{\partial^2 \vec{r}(s)}{\partial s^2}\right)^2 \tag{14}$$

The only contribution to the chain energy \mathcal{H} is due to its bending stiffness $\kappa = k_{\rm B}Tl_p$, and the chain conformation is not described in terms of discrete monomers and bonds connecting them, but in terms of a continuous curve $\vec{r}(s)$ following the chain contour, *s* being a coordinate along this contour. It is thought that eq 14 can be derived from an atomistic description by a suitable coarse-graining,⁴² and thus eq 14 is widely accepted (e.g., refs 1–20) as a valid model for semiflexible chains. Using eq 14, Odijk⁴ showed that for $D < l_p$ a chain follows essentially a straight path (but not parallel to the confining walls) over a length λ , the so-called deflection length

$$\lambda = (D^2 l_p)^{1/3}, \quad D < \lambda_p \tag{15}$$

and then the free energy cost of confinement is

$$\Delta F/k_b T \approx (L/\lambda) \ln(l_p/\lambda) = \frac{2}{3} (L/\lambda) \ln(l_p/D)$$
(16)

Because of these bending undulations, the chain is not propagating strictly parallel to the *xy*-plane, but typically would be inclined under an angle of order $\theta \approx D/\lambda \approx (D/l_p)^{1/3}$ relative to this plane.

Of course, the standard description eqs 14–16 is doubtful when the appropriate atomistic model of a stiff chain resembles the well-known rotational isomeric state (RIS) model,^{35,42,53} where bond lengths and bond angles are rigidly fixed, and there are three choices for the torsional angle. For example, for an alkane chain the energy difference between the gauche +,states (torsional angle $\varphi = \pm 120^{\circ}$) and the trans state ($\varphi = 0^{\circ}$) controls then the chain stiffness. The persistence length then is related to the typical distance of gauche states along the chain contour, while for very stiff chains trans states dominate. If such a model, as is appropriate for alkane-like polymers, describes the correct conformational statistics qualitatively correctly, eq

14 could result only when the coarse graining can be extended over length scales much larger than l_p , which makes it very doubtful whether then a regime where eqs 15 and 16 are valid would exist. Of course, biopolymers have a much more complicated chemical structure than alkane-like chains, and for them eq 14 could have a wider validity, but nevertheless it is of interest to explore the consequences of a model for stiff chains where angles between subsequent effective bonds are not continuously distributed, but only discrete angles can occur. For simplicity and for the sake of computational efficiency, we shall consider the self-avoiding walk (SAW) on the simple cubic lattice where stiffness is introduced by an energy penalty ε_h whenever the walk makes a 90° kink. Like eq 14, this is a drastic simplification of reality, but a very different approximation: while eq 14 ignores the fact that certain specific orientations of bonds of a semiflexible chain relative to each other are energetically preferred, the present model overemphasizes this fact, and it remains to be seen for which polymer which model is best.

In the following section, we introduce briefly the simulation method, while the third section presents our numerical results and the fourth section our conclusions.

2. SIMULATION DETAILS

We describe the semiflexible polymers as self-avoiding walks (SAWs) on the simple cubic lattice, where each effective monomer occupies a lattice site, multiple occupancy of lattice sites being forbidden, and the effective bond length l_b between nearest-neighbor occupied sites, the lattice spacing, henceforth will be used as our length unit. Since only bond angles $\theta = 0^{\circ}$, $\pm 90^{\circ}$ are possible on this lattice, the standard bond bending potential $U_b = \varepsilon_b(1 - \cos \theta)$ leads to the energy penalty ε_b if the walk makes a kink ($\theta = \pm 90^{\circ}$) while $U_b = 0$ for $\theta = 0^{\circ}$. Note that in an off- lattice model, where small angles are possible, one would find from this potential $U_b \approx \frac{1}{2}\varepsilon_b\theta^2$ compatible with eq 14, but small bond angles are excluded on the lattice. The partition sum then becomes a polynomial in the Boltzmann factor $q_b = \exp(-\varepsilon_b/k_{\rm B}T)$ for bond bending

$$Z_N(q_b, D) = \sum_{\text{config}} C_{N, N_{\text{bend}}}(q_b, D) q_b^{N_{\text{bend}}}$$
(17)

The sum over configurations includes all SAWs with *z*-coordinates of the effective monomers in the range $1 \le z \le D$; to realize the confinement, coordinates $z \le 0$ and $z \ge D + 1$ are forbidden. In eq 17, *N* is the number of effective monomers and N_{bend} is the number of kinks.

We note that the persistence length l_p can be extracted from the initial decay of the bond vector autocorrelation function (note that bond vectors \vec{a}_i are defined in terms of monomer coordinates \vec{r}_i as $\vec{a}_i = \vec{r}_{i+1} - \vec{r}_i$, i = 1, ..., N - 1)

$$\langle \vec{a}_i \cdot \vec{a}_{i+s} \rangle = \exp(-sl_b/l_p), \quad s < l_p/l_b, \quad \text{for } l_p/l_b \gg 1$$
(18)

noting $\langle a_i^2 \rangle = 1$ for our model. Equivalently, one can take $l_p/l_b = -1/\ln(\langle \cos \theta \rangle)$ where $\langle \cos \theta \rangle = \langle \vec{a}_i \cdot \vec{a}_{i+1} \rangle$. As discussed at length in the literature,^{39–41,46,47} the standard textbook definition to take l_p from the asymptotic decay $\langle \vec{a}_i \cdot \vec{a}_{i+s} \rangle \propto \exp(-sl_b/l_p)$ for $s \to \infty$ is wrong for self-avoiding walks, since (for $L \to \infty$) this asymptotic decay is not an exponential, but rather a power law,⁵⁴ $\langle \vec{a}_i \cdot \vec{a}_{i+s} \rangle \propto s^{-2(1-\nu)} \approx s^{-0.82}$.

Table 1. Estimates for Persistence Lengths, $l_p/l_b = -\ln(\langle \cos \theta \rangle)$, and $l_p/l_b \approx q_b^{-1}/4$ for Semiflexible Chains in d = 3 with Various Values of q_b



Figure 2. (a) Plot of the mean-square end-to-end distance $\langle R_{\parallel}^2 \rangle$ parallel to the walls, normalized by $N^{3/2} (=L^{3/2})$ plotted vs $D/I_p(q_b)$. The straight line shows the slope -1/2, predicted from eq 12. Many choices of q_b are included, as indicated. Only data extrapolated to $N \to \infty$ are included. (b) Same as (a), but for the mean-square gyration radius.



Figure 3. Scaling plot of $\langle R_{\parallel}^2 \rangle / (l_p^{2/5} N^{2\nu})$ versus $l_p^{1/5} N^{\nu} / D$ for $q_b = 0.4$ (a), 0.05 (b), 0.02 (c), and 0.01 (d). Several choices of D are included, as indicated. Here $\nu = 3/5$.

In the framework of a "nonreversal random walk" model, where immediate reversals of the random walk are forbidden, but otherwise excluded volume is completely neglected, one obtains $\langle \cos \theta \rangle = 1/[1 + 4q_b]$ and hence $l_p/l_b \approx q_b^{-1}/4 \approx \exp(\varepsilon_b/k_{\rm B}T)/4$. Table 1 compares this approximation with actual simulation results of the full model, taken from ref 46. It is seen that this simple approximation becomes accurate for $q_b \rightarrow 0$, as expected, unlike the two-dimensional case^{46,55,56} where irrespective of stiffness no Gaussian regime for the distribution of distances exists.

The simulation technique that is advantageous to use here is the pruned enriched Rosenbluth method (PERM).^{57–59} This chain growth algorithm with population control and depth-first implementation has been reviewed recently elsewhere⁵⁹ and has already been very successfully applied to confinement of flexible chains between parallel confining walls.⁵⁸ Aspects specific for the simulation of stiff chains can be found in refs 46 and 47. Accurate data for chain lengths up to $N = 80\,000$ have been obtained for $q_b = 1.0$ (flexible chains), 0.4, 0.2, 0.1, 0.05, 0.03, 0.02, 0.01, and 0.005. The values chosen for the distances between the confining slits were chosen as D = 8, 16, 30, 60,



Figure 4. Alternative scaling plot for stiff polymers in the Gaussian regime, $\langle R_{\parallel}^2 \rangle / (Nl_p)$ plotted vs $N / (Dl_p)$, for $q_b = 0.03$ (a), 0.02 (b), 0.01 (c), and 0.005 (d). Various values of *D* are included, as indicated.



Figure 5. Scaling plot of $\langle R_{\perp}^2 \rangle / (l_p^{2/5} N^{2\nu})$ versus $l_p^{1/5} N^{\nu} / D$ for $q_b = 0.4$ (a), 0.05 (b), 0.02 (c), and 0.01 (d). Several choices of D are included, as indicated.

and 120. Occasionally also other choices (D = 10, 20, 40, 60, and 80) were used. The present implementation of the algorithm did reproduce previous results for flexible chains⁵⁸ (as a special case for $q_b = 1.0$) very well.

3. RESULTS

As a first step, we estimate the ratios of the mean-square endto-end distances and gyration radii $\langle R_{\parallel}^2 \rangle / L^{3/2}$ and $\langle R_{g\parallel}^2 \rangle / L^{3/2}$, extrapolated to the limit of very long chains. Since eq 12 predicts that these ratios should follow a simple power law proportional to $(D/I_p)^{-1/2}$, we present these ratios in Figure 2. **Macromolecules**

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Figure 6. Rescaled monomer density profile, $(D + 1)\rho(z)$, plotted versus $\xi = z/(D + 1)$ for $q_b = 0.4$ (a), 0.05 (b), and 0.01 (c). Theoretical prediction $f_{\rho}(\xi) = 18.74[\xi(1 - \xi)]^{1/\nu}$ is also shown by the solid curve for comparison.



Figure 7. Rescaled distribution of chain ends, $(D + 1)\rho_{end}(z)$, at the distance z from a wall plotted versus $\xi = z/(D + 1)$ for $q_b = 0.4$ (a), 0.05 (b), and 0.01 (c). Theoretical prediction $g_{\rho}(\xi) = 4.78[\xi(1 - \xi)]^{0.865}$ is also shown for comparison (solid curve).

Having thus verified the final power law for R_{\parallel} vs *L* in Figure 1, which takes over after the last crossover, it is of interest to examine what happens when one examines somewhat shorter chains. From eq 11 we notice that this crossover occurs for $N^{3/5}/D$ being of order $l_p^{-1/5}$. So we expect that a plot of $\langle R_{\parallel}^2 \rangle / (N^{6/5} l_p^{2/5})$ versus this crossover variable $N^{3/5} l_p^{1/5}/D$ should be constant until one reaches this crossover point, before it starts to increase as $(N^{3/5}/D)^{1/2} l_p^{1/10}$, using again eq 12. While for $q_b = 0.4$ (where $l_p \approx l_b$) the scaling is almost

perfect, the scaling slightly but consistently deteriorates as l_p increases. Of course, this is expected, since for large l_p the range where excluded volume effects are visible shrinks, and more and more effects due to the Gaussian regime in Figure 1 come into play. In this schematic figure, we have assumed l_p of order 100, which leads to R^* of order 10^4 , so D of order 10^5 is needed in order to have a regime of three-dimensional SAW behavior, but then chain lengths of order 10^9 or larger would be needed, to enter the two-dimensional SAW behavior. On the other hand,

when smaller values of l_p are studied, as done in Figure 3, the various crossover regions of Figure 1 clearly are very close to each other. Recall that already for bulk stiff chains, where the two crossovers described by eqs 3–5 occur, there does not exist a simple scaling by which one can collapse the data on a master curves since there are two different scaling variables.^{46,47} This breakdown of a simple scaling comes over here.

Figure 4 tries then the scaling appropriate for the Gaussian regime, where free chains follow eq 4 rather than eq 5. So $\langle R_{\parallel}^2 \rangle$ is scaled by $l_p N$. To make it consistent with eq 12 for large N, we note that eq 12 yields $\langle R_{\parallel}^2 \rangle / (l_p N) = [N/(Dl_p)]^{1/2}$, and so we choose $N/(Dl_p)$ as an abscissa variable. Figure 4 shows three regimes: the initial strong increase (which splays out for different choices of D) is the rod-like regime. Of course, for rod-like chains oriented parallel to the walls confinement has little effect, so (at least for rather stiff chains, $q_b = 0.005$) we encounter essentially the same curve, shifted parallel along the abscissa. Then we have an almost horizontal regime, reflecting the Gaussian behavior, before the 2d SAW sets in. Thus, our data for large persistence lengths miss the three-dimensional SAW regime, while the data for medium persistence lengths miss the Gaussian regime. Thus, Figure 4 gives only evidence for 2 rather rounded crossovers instead of 3 crossovers: as expected, the much fewer decades on the abscissa in the simulation (in comparison with the schematic Figure 1) preclude a clear proof in favor of all predicted regimes.

In Figure 5, scaling plots of the mean-square transverse endto-end distances are given, plotting $\langle R_{\perp}^{2} \rangle / (l_{p}^{2/5} N^{2\nu})$ versus $N^{\nu} l_{p}^{1/5} / D$. The theoretical result $\langle R_{\perp}^{2} \rangle \approx D^{2}$ for small D corresponds to the slope -2 that is shown. In this case data scale nicely if one disregards the case where D is smaller than l_{p} .

Finally, Figures 6 and 7 address the rescaled monomer profiles and end monomer profiles across the film. Since in the fully flexible case (where l_p is not present) it has been found that some corrections to scaling can be incorporated if one scales $\langle R_{\parallel}^2 \rangle^{1/2}$ not with D but with D + 1, the distance between the two confining walls, we also use D + 1 instead of D here. Of course, in the scaling limit where both $N^{3/5} \to \infty$ and $D \to \infty$, this correction does not matter, but for not so large D (such as D = 10 and 20, as included here) such corrections may yield some improvement (although this is more like an empirical observation, without a deep theoretical explanation behind). One can see that the character of the distribution changes strongly with increasing polymer stiffness: for flexible chains these densities are strongly suppressed near the confining walls, and in fact the profiles can be fitted to simple empirical expressions⁵⁸

$$\rho(z) = \frac{1}{D+1} f\left(\frac{z}{D+1}\right),$$

with $f(\xi) = A[\xi(1-\xi)]^{(1/\nu)}$ (19)

with A = 18.74 and

$$\rho_e(z) = \frac{1}{D+1} f_e\left(\frac{z}{D+1}\right),$$

with $f_e(\xi) = A_e[\xi(1-\xi)]^{(\gamma-\gamma_1)/\nu}$ (20)

with $A_e = 4.78$, and γ , γ_1 are the exponents describing the partition function of a free SAW $(Z \propto N^{\gamma-1}\mu^{-N})$ and of a

"mushroom" with one end at the repulsive wall $(Z_1 \propto N^{\gamma_1-1}\mu^{-N}; \mu$ being the fugacity per monomer⁶⁰). The numerical values of the exponents are predicted as³³ $1/\nu \approx 1.70$ and⁶¹ $(\gamma - \gamma_1)/\nu \approx$ 0.81. Note that the scaling theory for polymers near surfaces (e.g. ref 60) implies that in the limit $D \to \infty$ one must have, for $N \to \infty$, $\rho(z) \propto z^{1/\nu}$, $\rho_e(z) \propto z^{(\gamma-\gamma_1)/\nu}$, but the success of eqs 19 and 20 suggest that these power laws hold essentially from the scale of the lattice spacing over the whole film. A closer look⁵⁸ has revealed that it is appropriate to remove some corrections to scaling by introducing a so-called "extrapolation length" $\delta(\approx$ 0.15) via redefining ξ as $\xi = (z + \delta)/(D + 1 + 2\delta)$, but this shall stay out of consideration here. In any case, Figures 6 and 7 show that eqs 19 and 20 no longer apply for semiflexible chains; rather, both $\rho(z)$ and $\rho_e(z)$ then are almost independent of z, when I_n becomes comparable to D.

Note that the density near the walls is proportional to the force per monomer.^{58,62} Thus, it is of interest to investigate the rescaled force per monomer, $fl_p^{7/3}$ (eq 13), extrapolated to $N \rightarrow \infty$, as a function of the stiffness (described by l_p) and film thickness *D*. Figure 8 shows that irrespective of l_p in the limit of $N \rightarrow \infty$ always the excluded volume behavior dominates, and hence $f \propto l_p^{1/3} D^{-1-1/\nu}$ as long as $D \gg l_p$.



Figure 8. Rescaled force $fl_p^{7/3}$ (extrapolated to $N \to \infty$) plotted vs D/l_p , including all the choices of q_b that have been studied. The straight line shows the theoretical slope $-1 - 1/\nu$.

4. CONCLUSIONS

In this paper we have discussed the scaling theory for semiflexible polymers confined between parallel repulsive walls a distance D apart, assuming good solvent conditions, and studied its validity using large scale Monte Carlo simulations of a simple lattice model to check some predictions of the theory. For the first time, both the excluded volume regime (valid if the radius R of the free chain exceeds the radius $R^* \propto l_p^{2}/l_b$, eq 6 and the regime of Gaussian behavior $(l_v \ll R < R^*)$ have been taken into account, and multiple crossovers were found (Figure 1). Because of the use of a model where bond angles cannot become small, the regime $D < l_p$ discussed much in the literature shows a different behavior than what is usually assumed; i.e., the "deflection length" (eq 15) does not control any chain properties here. As discussed in the Introduction, both the continuum approximation (on which the Kratky-Porod model, eq 14, is based) and the present model with a large bond angle of 90° (or other models with rigid bond lengths and discrete bond angles, such as the RIS model) are severe idealizations of actual macromolecules. While the numerical data presented here include the regime $D < l_p$ to some extent also, this regime is not emphasized much in our paper, since the significance of our numerical results in this regime for actual experiments due to the above caveats is somewhat uncertain.

However, for free chains the double crossover of the chain radii with chain length, from the rods to Gaussian chains (when the contour length L is comparable to the persistence length l_n and then from Gaussian chains to swollen, SAW-like coils (when L is comparable to $L^* = l_p^{3}/l_b^{2}$, the contour length corresponding to R^*) is very similar^{46,47} to corresponding experimental results,⁴⁷ and thus we feel that our results for $D > l_n$ are physically relevant and will be useful to understand experiments, and to clarify open theoretical problems. For example, in ref 23 it was claimed "that scaling theory fails to accurately describe the configurational probability distributions for extremely long chains". This criticism was based on Monte Carlo studies of a crude coarse-grained model for double stranded DNA, with $l_v = 50$ nm, while l_b (and the bond diameter) is taken to be 3 nm. However, it is clear that the simulation results of ref 23 do not reach the regime $L \gg L^*$, and hence it is mostly the regime of rods and Gaussian chains that is probed. In ref 22 it is emphasized that "Theoretical treatment of strong confinement for stiff chains in slit, however, is still not established", and it is suggested that eq 12 already holds if L exceeds a length Dl_p/l_b , which is not supported by our analysis either.

Experimentally, it is typically only the channel width D that is varied, keeping L fixed (as well as I_p , of course). For example, Bonthuis et al.²⁸ found for confined DNA evidence for a scaling of R_{\parallel} with D according to $R_{\parallel} \propto (R_{\rm bulk}/D)^{1/4}$ for about $2 < R_{\rm bulk}/D < 8.4$, while for thinner slits the ratio $R_{\parallel}/R_{\rm bulk}$ stayed constant at about 1.3, for a bulk radius of about $R_{\rm bulk} \approx 0.84 \ \mu m$. The scaling $R_{\parallel} \propto D^{-1/4}$ is compatible with eq 12, of course. The authors of ref 28 attribute the fact that R_{\parallel} does not change for $R_{\rm bulk}/D > 8.4$ to the Odijk⁴ regime, where no longer three-dimensional blobs can be formed. However, a similar behavior is also found in the present model, which does not have a "Odijk regime" (in the strict sense). Of course, the present model forms quasi-two-dimensional chains which simply scale as^{46,55}

$$R_{\parallel} \approx l_p (L_{\parallel}/l_p)^{3/4}$$
(21)

where L_{\parallel} is the length of that part of the chain contour that is parallel to the confining walls; note that for $l_p \gg D$ the parts of the contours that are oriented in the z-direction have a length of order *D* only and are separated by pieces of length⁵⁶ $l_{p,\parallel} \propto l_p^{-2}/D$ from each other. This argument shows that the part of the contour length oriented perpendicular to the confining walls $L_{\perp} \propto L(D/l_p)^2$, and hence $L_{\parallel} = L(1 - \text{const}(D/l_p)^2) \approx L$ for $D/l_p \ll 1$. Thus, also the present model predicts R_{\parallel} to be independent of *D* in the region of strong confinement.

One should also note that the sharp transition from the Daoud and de Gennes regime to the regime of strong confinement (where R_{\parallel} is independent of D) found by Bonthuis et al.²⁸ is not confirmed by the recent data of Tang et al.,³⁰ we find a much more gradual crossover. This is compatible with the results presented here.

Thus, we hope that the present study will be useful for the interpretation of future experimental studies of this problem as well.

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Notes

The authors declare no competing financial interest.

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NOTE ADDED IN PROOF

In our treatment (Figure 1, eqs 4 and 6) the simplifying approximation was made to neglect residual effects of excluded volume interactions in the Gaussian regime completely. Of course, whenever the persistence length l_p in our model is large but finite, i.e. q_b small but still nonzero, we do expect some enhancement of linear dimensions of the chain relative to the Gaussian results.^{34,35,50} For contour lengths in the regime where L has not yet exceeded l_p^3/l_b^2 very much, the effects of excluded volume can be still treated perturbatively, and hence we expect already for an unconfined semiflexible chain (as studied by us earlier^{46,47}) that the expansion factor $\langle R^2 \rangle / (2l_n L)$ exceeds unity, and this deviation increases with increasing q_b . This is in fact borne out by the numerical data for unconfined chains (Figure 9a,b). Therefore as long as $q_b > 0$ there is never a strictly horizontal part in the plot of the expansion factor versus L/l_{m} but rather there occurs a minimum in the slope and this minimum gets smaller the smaller q_b . The latter feature remains also true for confined chains (Figure 9c). We are very grateful to an anonymous referee on illuminating remarks on this point.



Figure 9. (a) Expansion factor $\langle R^2 \rangle / (2l_pL)$ plotted vs L/l_p for unconfined semiflexible chains. Various choices of q_b are included, as indicated. (b) Plot of these expansion factor for $L/l_p = 100$ vs q_b . The best-fit straight for the data is given by: $\langle R^2 \rangle / (2l_pL) = 1 + 1.55q_b$ as $q_b \rightarrow 0$. (c) Rescaled mean square end-to-end distance in the direction parallel to the wall, $\langle R_{\parallel}^2 \rangle / (2l_pL)$, plotted vs, L/l_p for D = 80. Note that the curves near $L/l_p = 100$ become flatter when q_b decreases: similar as for the chains (a), a perfect scaling in this crossover regimes cannot be expected.