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Simulation Study on the Extension of Semi-flexible Polymer Chains in Cylindrical Channel

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Abstract The scaling relations among the mean end-to-end distance of polymer along the channel $\langle R_{\parallel} \rangle$, the polymer length N , and the effective diameter of channel D_e were investigated for flexible and semi-flexible polymer chains confined in long cylindrical channels. For the flexible polymer chain, scaling relation $\langle R_{\parallel} \rangle \sim ND_e^{-0.7}$ was found in the classic de Gennes regime at $l_p^2/b < D_e < R_g$ with l_p the persistence length, b the bond length, and R_g the radius of gyration of polymer. For the semi-flexible polymer, $\langle R_{\parallel} \rangle \sim ND_e^{-1}$ in the transition regime $l_p < D_e < xl_p$ ($x > 1$) and $\langle R_{\parallel} \rangle \sim D_e^{-0.7}$ in the classic de Gennes regime at larger $D_e > xl_p$ were observed. The simulation results revealed that the scaling relation in the transition regime was due to the rod-like behavior of the semi-flexible polymer in the small regime $l_p < D_e < xl_p$.

Keywords Semi-flexible polymer; Cylindrical channel; Conformation; Scaling relation; Monte Carlo simulation

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INTRODUCTION

The phenomenon that biopolymers are confined in micro space is ubiquitous, such as packaging of DNAs in chromosome,^[1] the proteins in membrane,^[2] and the transfer of viral genes between cells and the passage of RNA through nuclear pores and cell membranes.^[3] The static properties of polymer chains in a confined environment are different from those in solution, and have received extensive attentions from theories,^[4,5] experiments,^[6,7] and simulation calculations.^[8–12] Cylindrical channels, *e.g.* the carbon nanotubes, as well as square channels and parallel slit channels, facilitate the study of DNA at the monomer level.^[13–16] Extensive research has been carried out on the static properties of polymer chains confined in cylindrical channels.^[17–19]

The conformational property of semi-flexible polymer chains is an important research content in polymer physics. When a polymer is confined in a cylindrical channel of diameter D , the conformational property of the polymer is related to the channel diameter D .^[20,21] At weak restriction with D much larger than the radius of gyration R_g of the polymer, the behavior of the polymer is the same as that in solution, while at strong restriction with D much smaller than the persistence length l_p , the bending potential of the polymer plays a dominant role and this regime is called the

Odiijk regime. It is known that the deflection length is much smaller than l_p in the Odiijk regime, so the polymer chain can be treated as a rod.^[22]

Between these two limitations, there exists the classic de Gennes regime where the transverse dimension of polymer equals the diameter D . Therefore, the macroscopic conformational size of the self-avoiding polymer is represented by the end-to-end distance parallel to the channel, $R_{\parallel}$. And the free energy of the semi-flexible polymer can be expressed as^[20,21]

$$\frac{F(R_{\parallel})}{k_B T} = \frac{R_{\parallel}^2}{Nbl_p} + \frac{wb^2N^2}{D^2R_{\parallel}} \quad (1)$$

where N is the chain length, b is the bond length, w is the width of monomer, k_B is the Boltzmann constant, and T is the system temperature. The first term describes the configurational entropy of the polymer, which attempts to curl the configuration and reduce the size. The second term is the contribution of the excluded volume (EV) effect, which tends to stretch the polymer. At the equilibrium state, the free energy reaches a minimum value, so one can obtain the following scaling relation^[21]

$$R_{\parallel} \sim D^{-2/3} Nbl_p^{1/3} w^{1/3} \quad (2)$$

The equilibrium size $R_{\parallel}$ of the polymer chain in the classic de Gennes regime is then in proportion to the chain length N and decreases with the increasing diameter D at a power exponent of $-2/3$.^[8,11,18,21]

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The equilibrium size $R_{||}$ can also be described by the blob picture introduced by de Gennes where a polymer chain consists of mutually exclusive spherical blobs.^[23] Each blob corresponds to a free or self-avoiding chain with g monomers, and blob's energy is approximately $k_B T$. Because of the geometrical limitation of the channel, the size of blobs is equivalent to the size of the channel D and the polymer chains can only be sequentially arranged in the channel. Therefore, the polymer chain in the channel can be regarded as a molecular chain consisting of N/g blobs with diameter D .^[24,25] One can obtain the number of monomers in each blob as $g \sim (D/b)^{1/\nu}$ and the size of the polymer chain in the channel from^[26]

$$R_{||} \sim D(N/g) \sim Nb(D/b)^{1-1/\nu} \quad (3)$$

For the three-dimensional (3D) self-avoiding polymer chain, the Flory exponent ν equals 0.6, and then the scaling relation (Eq. 3) obtained from the blobs theory is consistent with that (Eq. 2) obtained from the free energy analysis. When using a more accurate Flory exponent value $\nu = 0.588$,^[27] one can obtain $R_{||} \sim ND^{-0.7}$ for the confined polymer chain.^[8]

The scaling relation of $R_{||} \sim D^{-2/3}$ or $R_{||} \sim D^{-0.7}$ has been proven theoretically^[28,29] as well as by simulations.^[8,9,11,18,24] However, experiment showed that the behavior of the extension of DNA chain in this regime followed a power law in the form of $D^{-0.85}$.^[6] It was suggested that Monte Carlo (MC) simulation studies of confined polymer chain might be essential to clarify the situation.^[6] Simulation also found $R_{||} \sim D^{-1}$ at smaller D for semi-flexible polymers.^[8,21,30,31] It is argued that the confined semi-flexible chain behaves as an ideal chain in the absence of EV effect in this special situation.^[30,31] For an ideal chain, one gets the number of monomers $g \sim D_e^2$ in one blob of size D_e and therefore obtains the extension of chain as $R_{||} \sim (N/g)D_e \sim ND_e^{-1}$. Another suggestion for the scaling $R_{||} \sim D^{-1}$ in the transition regime is that the fraction of aligned segments close to the channel walls is substantial and the extension is significantly affected by the effect of segment alignment.^[21] The origin of this scaling relation still remains an open question and underlying physics is not clear yet.^[8]

In this work, the conformational property of polymers in cylindrical channels is studied by using off-lattice dynamic MC method. We have investigated the influence of chain stiffness on the extension of polymers in cylindrical channels. Different scaling relations are observed for flexible polymer chain and semi-flexible polymer chain in the regime between the strong confined Odijk regime at very small $D_e \ll l_p$ and weak confined regime at large $D_e \gg R_g$. For the flexible polymer chain, we find only one scaling relation $\langle R_{||} \rangle \sim ND_e^{-0.7}$ in the classic de Gennes regime $l_p^2/b < D_e < R_g$ for the mean end-to-end distance $\langle R_{||} \rangle$ along the axial direction. As for the semi-flexible polymer chain, we find two scaling relations: $\langle R_{||} \rangle \sim ND_e^{-1}$ in the transition regime $l_p < D_e < xl_p$ ($x > 1$) and $\langle R_{||} \rangle \sim D_e^{-0.7}$ in the classic de Gennes regime at larger $D_e > xl_p$. We reveal that the scaling relation in the transition regime is due to the rod-like behavior of the semi-flexible polymer in the small channel with $l_p < D_e < xl_p$.

SIMULATION MODEL AND METHOD

Off-lattice MC simulations are carried out for a coarse-grained bead-spring polymer chain confined in an infinitely long cylindrical channel. The polymer chain of polymer length N consists of N identical bonds or $N+1$ homogeneous monomers numbered from 0 to N . The contour length is $L = Nb$ with b the mean bond length.

We consider the bond potential, repulsive interaction between non-bonded monomers, and bending potential for the polymer chain. The finitely extensible non-linear elastic (FENE) potential^[32]

$$U_{\text{FENE}}(r_b) = \begin{cases} -\frac{k_F}{2}(r_{\max} - r_{\text{eq}})^2 \ln \left[1 - \left(\frac{r_b - r_{\text{eq}}}{r_{\max} - r_{\text{eq}}} \right)^2 \right], & r_{\min} < r_b < r_{\max} \\ \infty, & \text{otherwise} \end{cases} \quad (4)$$

is adopted for the bond potential, where k_F is elastic strength, r_b is the bond length between two sequential monomers along the polymer chain, r_{eq} is the equilibrium bond length, and $r_{\max}$ is the maximum bond length. The minimum bond length is $r_{\min} = 2r_{\text{eq}} - r_{\max}$. Simulation shows that the mean bond length b is close to r_{eq} , and it is roughly independent of k_F .^[33] The interaction between non-bonded chain monomers is purely repulsive and is described by the Weeks-Chandler-Andersen (WCA) potential^[34]

$$U_{\text{WCA}}(r_{ij}) = \begin{cases} 4\varepsilon_{\text{PP}} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right], & r_{ij} < 2^{1/6}\sigma \\ 0, & r_{ij} \geq 2^{1/6}\sigma \end{cases} \quad (5)$$

Here, ε_{PP} is the interaction strength between the monomers, σ is the diameter of monomer, and r_{ij} is the centroid distance between the i^{th} and j^{th} monomers.

The stiffness of the polymer chain is represented by the bending energy. The bending energy, associated with the angle θ formed by two adjacent bonds, has the following form^[35]

$$U_{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \quad (6)$$

Here k_θ is the bending modulus and θ is the bond angle between two consecutive bonds. In the simulation, $\theta_0 = \pi$ is set, i.e., the potential energy of the bending energy is the lowest in the case of stretching. We can change the bending modulus k_θ to adjust the stiffness of the chain, and the chain stiffness can be described by the persistence length l_p .

The diameter of channel is represented by D . In the simulation, a channel with a finite length of L_x along the axial direction is used. To eliminate the size effect due to the finite length L_x , we set $L_x > L$ in the simulation. Periodic boundary condition is adopted along the axial direction to mimic an infinitely long channel. The interaction between polymer and channel is simply purely repulsive with the WCA potential

$$U_{\text{WCA}}(d_i) = \begin{cases} 4\varepsilon_{\text{PT}} \left[\left(\frac{\sigma}{d_i} \right)^{12} - \left(\frac{\sigma}{d_i} \right)^6 + \frac{1}{4} \right], & r < 2^{1/6}\sigma \\ 0, & r \geq 2^{1/6}\sigma \end{cases} \quad (7)$$

Here d_i is the distance from the centroid of the i^{th} monomer

to the wall of the channel. The interaction strength between the polymer and the channel is denoted as ε_{PT} .

The units for length and energy are set as σ and $k_{\text{B}}T$, respectively, where k_{B} is the Boltzmann constant, and T is the absolute temperature of system. The elastic coefficient $k_{\text{F}} = 200$, the maximum bond length $r_{\text{max}} = 1.3$, the equilibrium bond length $r_{\text{eq}} = 0.8$, and interaction strength $\varepsilon_{\text{PP}} = \varepsilon_{\text{PT}} = 1$ are used in the simulation. Here the relatively large value $k_{\text{F}} = 200$ results in a small bond length fluctuation,^[33] and our simulation shows that the mean bond length is roughly independent of k_{F} as long as it is not too large or not too small.

For the sake of convenience, we set the axial direction of the channel as x . First, we generate a single polymer chain in the channel with the bond length equal to the equilibrium bond length r_{eq} and no overlap between monomers. Then we randomly select a monomer and move it a small step $d\vec{r} = dx\vec{i} + dy\vec{j} + dz\vec{k}$, where dx , dy , and dz are mutually independent random values in the interval $[-\Delta, \Delta]$. A small simulation step $\Delta = 0.1$ is used. The Metropolis algorithm is used to determine whether the move is accepted or not. The Metropolis method is a random walk of importance weight, which travels through all possible configurations according to the Boltzmann distribution. According to the Metropolis algorithm, the acceptance probability of the move is $p = \min[1, \exp(-\Delta E/k_{\text{B}}T)]$, where ΔE is the energy difference due to the move. The simulation time unit is MC step (MCS). In one MCS, all monomers attempt to move once in average. The equilibrium time of the polymer chain during the simulation is about $100N^2$ MCSs, and the statistical time is about 10^7 MCS.

In this work, we study the influence of the diameter D of the channel and the bending modulus k_{θ} on the conformation of the polymer. The simulation results are averaged over at least 1000 independent samples. The standard deviation of the simulation results is small and can be ignored. Our simulation shows the mean bond length $b \approx r_{\text{eq}} = 0.8$ and it is roughly independent of the diameter D as well as the bending modulus k_{θ} .

RESULTS AND DISCUSSION

Effective Diameter of Channel

Due to the repulsion of channel surface and the depletion effect of polymer, the diameter for accommodating the polymer chain is smaller than the physical diameter of the channel. We have simulated the equilibrated monomer distribution of the polymer chain in the channel, and calculated the radial distribution of monomer density ρ , $\rho = \frac{dN}{2\pi r dr}$, where dN is the number of monomers in the ring from r to $r + dr$. Fig. 1 shows the variation of ρ/ρ_0 with the distance d ($d = D/2 - r$) from the channel surface, where $\rho_0 = \frac{N}{\pi(D/2)^2}$ is the average monomer density uniformly distributed in the channel. For different channels and different stiffnesses of chain, the monomer density is always close to 0 for $d < 0.85$, indicating that monomers are forbidden in space with $d <$

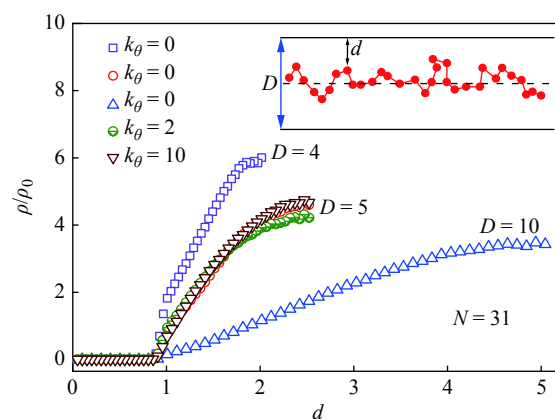


Fig. 1 Plot of the radial density ρ for polymer in channel versus the distance d from the channel surface. ρ_0 is the average monomer density uniformly distributed in the channel. Here polymer length is $N = 31$. The inset shows a polymer chain in a channel, where the dashed line represents the center of the channel and d is the distance from the monomer to the channel surface. The standard errors of the simulation data shown in the plot as well as in the following plots are of the same size as that of symbols.

0.85. We define the diameter of the channel that can be reached by the polymer chain is the effective channel diameter, and we get the effective diameter

$$D_e = D - 1.7 \quad (8)$$

Due to the repulsion of channel surface and the depletion effect of polymer, the probability of the polymer chain at the center of the channel is the greatest. So we find ρ/ρ_0 increases with d as shown in Fig. 1. For the same reason, there are more monomers at the center for small channel, therefore we can see that ρ/ρ_0 at the center of channel decreases with the increasing channel size D .

Statistical Properties of Polymer Chain

We have first calculated the statistical mean end-to-end distance along the axial direction of the channel, $\langle R_{\parallel} \rangle$, for the flexible polymer chain ($k_{\theta} = 0$) confined in cylindrical channel. Fig. 2 shows the variation of $\langle R_{\parallel} \rangle$ with the effective diameter D_e for the flexible polymer with length $N = 191$. For the flexible polymer in dilute solution, we have $l_p \approx 1.51$ and $R_g \approx 9.2$ for the polymer with length $N = 191$. The persistence length l_p is the projection length of the end-to-end vector $\vec{R}$ on the first bond vector $\vec{b}_1$, i.e.,

$$l_p = \vec{R} \cdot \vec{b}_1 / b_1 \quad (9)$$

under the limit that the polymer is infinitely long.^[36,37] The persistence length l_p is independent of polymer length and it is calculated based on the polymer with length $N = 127$ in this work. In the Odijk regime ($D_e \ll l_p$) where the effective diameter of channel is much smaller than the persistence length, the polymer chain is in an unfolded long strip conformation,^[38] and the polymer statistic size satisfies the Odijk formula^[8,39]

$$\langle R_{\parallel} \rangle \sim L \left(1 - \alpha_{\parallel}^{\text{odijk}} D_e^{\frac{2}{3}} / l_p^{\frac{2}{3}} \right) \quad (10)$$

with L the contour length of the polymer chain and $\alpha_{\parallel}^{\text{odijk}} = 0.1701$.^[39,40] Our simulation results can be well described by

the Odijk formula as shown by the dotted red line in Fig. 2. However, there is an obvious deviation between the prediction of the Odijk regime and the measured data for $D_e \lesssim l_p$. This is attributed to the presence of backfolds.^[21] On the other hand, when D_e is much larger than R_g , $\langle R_{||} \rangle$ gradually approaches to a constant $\langle R_{||} \rangle_0$, indicating that the channel does not affect the conformational property of the polymer and the polymer chain is in an unrestricted free state.

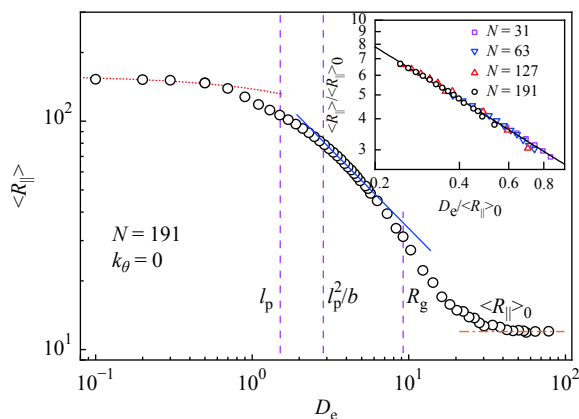


Fig. 2 Log-log plot of the mean end-to-end distance $\langle R_{||} \rangle$ versus the effective diameter D_e for the completely flexible polymer chain of length $N = 191$. The dotted line is the Odijk formula, the slope of the straight blue line is -0.7 , the three vertical dashed lines represent the persistence length l_p , the square persistence length l_p^2/b , and the radius of gyration R_g , respectively, and the horizontal dotted dash line indicates $\langle R_{||} \rangle_0$ of the polymer in solution. The inset shows log-log plot of $\langle R_{||} \rangle / \langle R_{||} \rangle_0$ versus $D_e / \langle R_{||} \rangle_0$ for the polymers with lengths $N = 31, 63, 127$, and 191 in the classic de Gennes regime ($l_p^2/b < D_e < R_g$).

In the classic de Gennes regime ($l_p^2/b < D_e < R_g$), the polymer chains form impenetrable blobs one after another.^[23] We find a scaling relation $\langle R_{||} \rangle \sim D_e^{-0.7}$ for $N = 191$ in the classic de Gennes regime. The inset of Fig. 2 shows the variation of $\langle R_{||} \rangle / \langle R_{||} \rangle_0$ with $D_e / \langle R_{||} \rangle_0$ for the polymer chains with polymer lengths $N = 31, 63, 127$, and 191 in the classic de Gennes regime, where $\langle R_{||} \rangle_0$ is the value of $\langle R_{||} \rangle$ of the polymer chain in solution. All the data of different polymer lengths in the classic de Gennes regime almost fall on the same line with a slope of -0.7 , that is, our simulation results show the relation $\langle R_{||} \rangle / \langle R_{||} \rangle_0 \sim (D_e / \langle R_{||} \rangle_0)^{-0.7}$ for the flexible polymer in the classic de Gennes regime. Therefore, we obtain the scaling relation between the polymer chain size and the effective diameter of channel D_e as $\langle R_{||} \rangle \sim \langle R_{||} \rangle_0^{1.7} D_e^{-0.7}$ in the classic de Gennes regime. Given $\langle R_{||} \rangle_0 \sim N^{0.588}$ for a self-avoiding polymer chain, we can get the following relation

$$\langle R_{||} \rangle \sim N D_e^{-0.7} \quad (11)$$

for the extension of the flexible polymer chain in the classic de Gennes regime. This scaling relation is the same as Eq. (3) derived from the free energy analysis as well as the blob theory.

In addition, we can see that there are two transition regimes between the Odijk regime and the classic de Gennes regime, and between the classic de Gennes regime and the

free regime. Our simulation does not show any scaling relation in the two transition regimes for the flexible polymers.

For the semi-flexible polymer chain, both the persistence length l_p and the radius of gyration R_g of the polymer chain are dependent on the bending moduli k_θ . We have calculated l_p , l_p^2/b , and R_g for the polymer chain with different bending modulus k_θ , and the results are presented in Fig. 3 for the polymer of length $N = 127$ as an example. We can see that l_p , l_p^2/b , and R_g increase with increasing k_θ . We find l_p is almost in linear proportion to the bending modulus k_θ , l_p^2/b is proportional to the square of k_θ , while the radius of gyration R_g increases the most slowly with increasing k_θ . We find the width of the classic de Gennes regime ($l_p^2/b < D_e < R_g$) also decreases with increasing k_θ and the regime disappears at large k_θ where $l_p^2/b > R_g$ occurs. For the semi-flexible polymer chain with length $N = 127$, the classic de Gennes regime exists only for $k_\theta < 2$ as shown in Fig. 3 as $l_p^2/b < R_g$ only appears for $k_\theta < 2$.

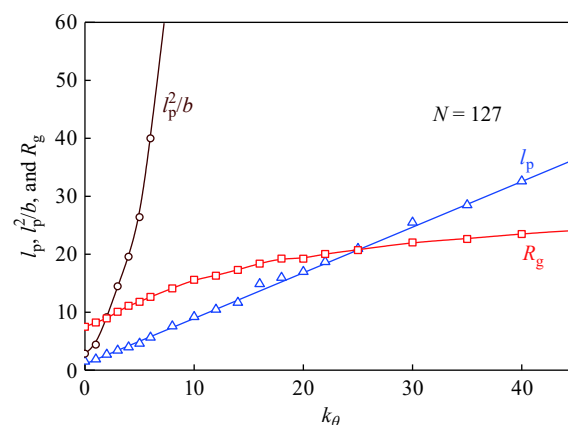


Fig. 3 Dependence of the persistence length l_p , the square persistence length l_p^2/b , and the radius of gyration R_g of the polymer chain on the bending modulus k_θ . Polymer length is $N = 127$. Solid lines are guides for the eyes.

Fig. 4 shows the dependence of $\langle R_{||} \rangle$ on the effective diameter D_e for the semi-flexible polymers with length $N = 127$ and $N = 191$ and bending modulus $k_\theta = 2$. We find $l_p^2/b \sim R_g$ for $N = 127$ and $l_p^2/b < R_g$ for $N = 191$. For both cases, the dependence of $\langle R_{||} \rangle$ on D_e can be well fitted by the Odijk formula when D_e is much smaller than l_p , as shown by the solid black line in Fig. 4. Above the Odijk regime, we find $\langle R_{||} \rangle \sim D_e^{-1}$ for the semi-flexible polymer chain when $D_e > l_p$. As shown in the inset of Fig. 4, the curves $\langle R_{||} \rangle / L$ versus D_e / l_p of different chain lengths overlap when $l_p < D_e < 5l_p$. Since the contour length L of the polymer chain is proportional to the number of bonds N , the relation between $\langle R_{||} \rangle$ and D_e of the semi-flexible polymer chain can be expressed as

$$\langle R_{||} \rangle \sim N D_e^{-1} \quad (12)$$

We find this special regime starts from $D_e = l_p$, but the width of this regime increases with increasing polymer length. For example, the regime ends at about $3l_p$ for a short polymer length $N = 31$ as shown in the inset of Fig. 4. The regime was defined as the transition regime.^[8,21] The observed width for

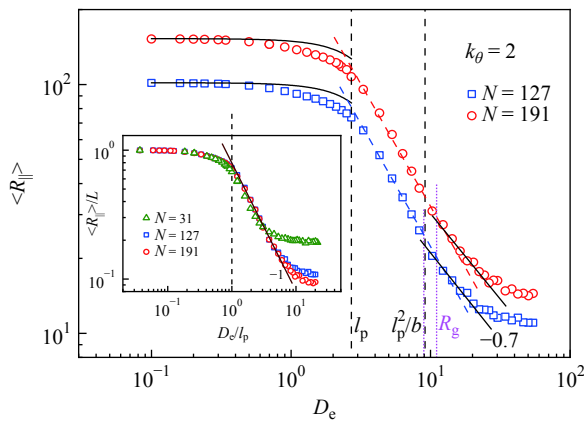


Fig. 4 Log-log plot of $\langle R_{||} \rangle$ versus the effective diameter D_e for the semi-flexible polymer chains ($k_\theta = 2$) of polymer chain length $N = 127$ and 191. The two vertical dashed lines represent the persistence length l_p and the square persistence length l_p^2/b , respectively, and the two vertical dotted lines represent the radius of gyration R_g of the polymer chain. The solid curves are the Odijk formula, and the slopes of the dashed straight lines and solid straight lines are -1 and -0.7 , respectively. The inset shows the relation between $\langle R_{||} \rangle/L$ and D_e/l_p for polymers of length $N = 31, 127$, and 191.

the transition regime is wider than $l_p < D_e < 2l_p$ for polymer in square nanochannel.^[8]

Above the transition regime, we find $\langle R_{||} \rangle \sim D_e^{-0.7}$, indicating that the semi-flexible polymer enters the classic de Gennes regime or the extended de Gennes regime, in agreement with other simulation results.^[8,21] However, the classic de Gennes regime of the semi-flexible polymer is different from that of the flexible polymer in the following two points. One is that the region with the scaling relation $\langle R_{||} \rangle \sim D_e^{-0.7}$ for the semi-flexible polymer is obviously different from the flexible polymer ($l_p^2/b < D_e < R_g$). The other is that the relation between $\langle R_{||} \rangle$ and N is not clear for the semi-flexible polymer from our simulation results, *i.e.* the polymer length-dependent behavior of $\langle R_{||} \rangle$ is different for these two kinds of polymers.

We have also examined the conformational properties of semi-flexible polymers with higher k_θ for $N = 127$ where $l_p^2/b > R_g$ occurs since l_p^2/b increases much faster than R_g as shown in Fig. 3. Fig. 5 shows the dependence of $\langle R_{||} \rangle$ on the effective diameter D_e for the semi-flexible polymer chain of $N = 127$ with different bending moduli $k_\theta = 2, 4$, and 6. The persistence lengths l_p are about 2.70, 3.96, and 5.66 for $k_\theta = 2, 4$, and 6, respectively. The corresponding values of w/l_p are 0.37, 0.25, and 0.18, respectively, which are slightly larger than $w/l_p = 0.05\text{--}0.2$ used in previous simulation,^[21] which means the polymer chain in our simulation is relatively flexible. We find the scaling relation $\langle R_{||} \rangle \sim D_e^{-1}$ holds for these k_θ s, but the width of the regime decreases with increasing k_θ . Again, we find $\langle R_{||} \rangle \sim D_e^{-0.7}$ at large D_e for different k_θ s. The separation for the two regime is about $D_e = 10$, corresponding to $3.7l_p, 2.5l_p$, and $1.8l_p$ for $k_\theta = 2, 4$, and 6, respectively.

In short, our simulation results show that the extension of the semi-flexible polymers in cylindrical channel has the same scaling relations. Between the strong confined Odijk

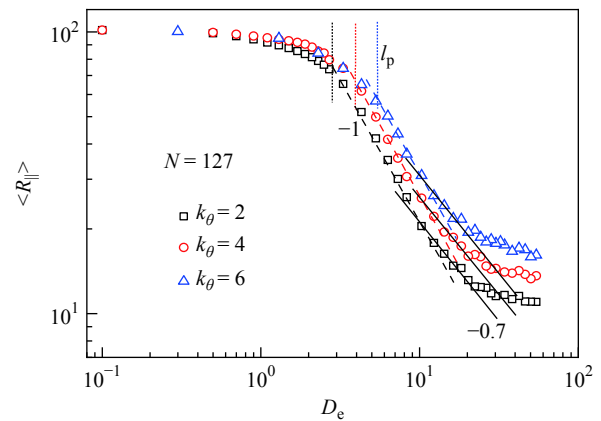


Fig. 5 Log-log plot of $\langle R_{||} \rangle$ of semi-flexible polymer chain of length $N = 127$ with $k_\theta = 2, 4$, and 6 versus the effective diameter D_e of channel. The three vertical dotted lines represent the persistence length l_p . The dashed straight lines with the slope of -1 and solid straight lines with the slope of -0.7 are guides for the eyes.

regime and weak confined regime, we find two scaling relations: $\langle R_{||} \rangle \sim ND_e^{-1}$ in the transition regime $l_p < D_e < xl_p$ ($x > 1$) and $\langle R_{||} \rangle \sim D_e^{-0.7}$ in the classic de Gennes regime at larger $D_e > xl_p$. The width of the transition regime $(x - 1)l_p$ is dependent on the polymer length N and chain stiffness. Some studies pointed out that there was an extended de Gennes regime between the Odijk regime and the classic de Gennes regime and the scaling relation in this regime was the same as that in the classic de Gennes regime.^[8,11,41] Therefore one cannot distinguish these two regimes from the scaling behavior. Wang *et al.* also pointed out there was a transition regime with $\langle R_{||} \rangle \sim D_e^{-1}$ below the extended de Gennes regime.^[8] Our simulation confirms that there is a transition regime with different scaling behaviors from that in the classic de Gennes regime.^[21,30]

The scaling relation $\langle R_{||} \rangle \sim ND_e^{-1}$ (Eq. 12) was also found for the semi-flexible polymer chain in square channel^[8,21] as well as in cylindrical channel.^[30,31] However, the origin of this scaling relation remains an open question.^[8] It was argued that the confined semi-flexible chain behaves as an ideal chain with the absence of EV effect.^[30,31] In that simulation, the regime for exponent -1 occurred near $D_e = 1.5l_p$,^[30] which corresponds to $g = 45$ in one blob for the case $l_p = 20$. However, $g = 45$ is not in the ideal chain region from the simulation results; instead, it is still in the rod-like chain regime.^[31] It was also pointed out that the scaling $\langle R_{||} \rangle \sim D_e^{-1}$ in the transition regime might be due to the substantial fraction of aligned segments close to the channel walls and the extension is significantly affected by the effect of segment alignment.^[21]

We have checked the mean end-to-end distance $\langle R \rangle$ of polymer chain in dilute solution for flexible and semi-flexible chains. Fig. 6 presents the dependence of $\langle R \rangle$ on N for polymer chains with $k_\theta = 0$ and 4. We find scaling relation $\langle R \rangle \sim N^{0.6}$ is valid for both small and large N for the flexible chain with $k_\theta = 0$, confirming the classical scaling exponent for self-avoiding polymer chain. In comparison, for the semi-flexible chain with $k_\theta = 4$, we find the scaling exponent

in the small N regime is large and $\langle R_g \rangle \sim N^{0.6}$ is valid for relatively large $N > N^* = 17$. This is in agreement with the simulation results for wormlike chain.^[8] The length $N^* = 17$ separates the semi-flexible polymer with $k_\theta = 4$ into two regimes: a rod-like chain regime at $N < N^*$ and a coil-like chain one at $N > N^*$. Nevertheless, we do not observe ideal chain behavior with exponent 0.5 for the semi-flexible polymer. Our results thus show that the scaling relation (Eq. 12) does not result from the ideal chain behavior of semi-flexible polymer in dilute solution.

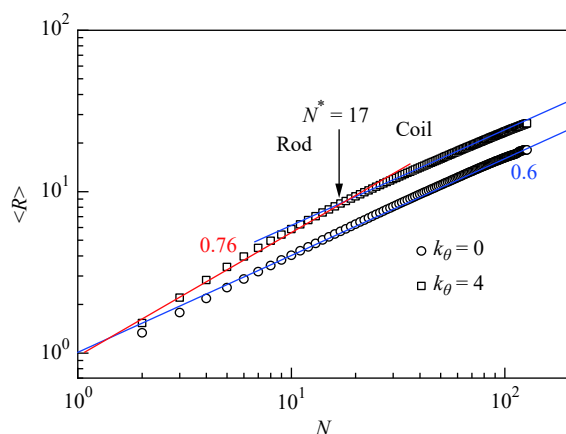


Fig. 6 Log-log plot of mean end-to-end distance $\langle R \rangle$ versus polymer length N for polymer chains with $k_\theta = 0$ and 4 in dilute solution. Straight lines of the slope 0.6 (blue) and 0.76 (red) are guides for the eyes.

However, it would be interesting to compare the EV effect for the flexible polymer chain and the semi-flexible one in cylindrical channels. To ensure $\langle R_{||} \rangle$ for the two type polymers are similar, we choose $D_e = 4$ and $k_\theta = 0$ for the flexible polymer and $D_e = 7$ and $k_\theta = 4$ for the semi-flexible polymer. Here the flexible polymer is in the classic de Gennes regime with $\langle R_{||} \rangle \sim D_e^{-0.7}$ at $D_e = 4$, while the semi-flexible polymer with $k_\theta = 4$ is in the transition regime with $\langle R_{||} \rangle \sim D_e^{-1}$ at $D_e = 7$. Fig. 7 shows the snapshots for the flexible polymer and the semi-flexible polymer with the same length $N = 127$. It is clear to see that the EV effect is weaker for the semi-flexible polymer since the non-bonded monomer-monomer distance is larger in the semi-flexible polymer.

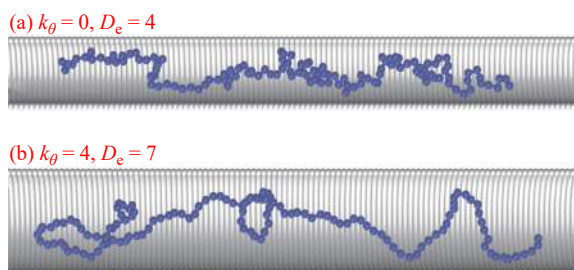


Fig. 7 Snapshots of polymer of length $N = 127$ inside cylindrical channel for (a) $k_\theta = 0$ and $D_e = 4$ and (b) $k_\theta = 4$ and $D_e = 7$

The mean end-to-end distance $\langle R \rangle$ and the mean parallel component of end-to-end distance $\langle R_{||} \rangle$ are calculated for the

confined polymer inside the cylindrical channel. Fig. 8 shows the dependence of $\langle R \rangle$ and $\langle R_{||} \rangle$ on the polymer length N . For the flexible polymer with $k_\theta = 0$, $\langle R_{||} \rangle$ increases linearly with N as indicated by Eq. (11), while $\langle R \rangle$ increases with N in the scaling law $\langle R \rangle \sim N^{0.6}$ in small N region where the confinement is weak and it increases linearly with N in large N region where the confinement is strong. These results are obvious for a self-avoiding flexible polymer chain.

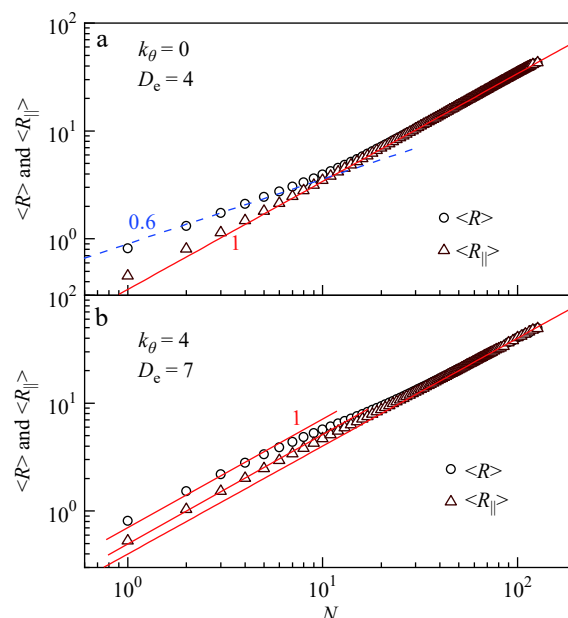


Fig. 8 Dependence of $\langle R \rangle$ and $\langle R_{||} \rangle$ on polymer length N for the confined polymer inside cylindrical channel for (a) $k_\theta = 0$ and $D_e = 4$ and (b) $k_\theta = 4$ and $D_e = 7$. The solid red line with the slope 1 and the dashed blue line with the slope 0.6 are guides for the eyes.

However, we find $\langle R \rangle \sim N$ in both the small N regime and the large N regime for the semi-flexible one with $k_\theta = 4$ in the transition regime. Although the relation is the same, the physical mechanism is somewhat different for these two behaviors. The behavior $\langle R \rangle \sim N$ at small N is due to the rod-like behavior of polymer chain,^[42] whereas the behavior $\langle R \rangle \sim N$ at large N is due to the confinement of the channel. For large N , the polymer is already flexible since $L \gg l_p$. At moderate N , there is a transition from the rod-like behavior to flexible chain behavior. However, we do not observe ideal chain behavior with $\langle R \rangle \sim N^{0.5}$ from the simulation. In addition, we can see $\langle R_{||} \rangle \sim N$ in both small N regime and large N regime. This indicates that the origin for exponent -1 in Eq. (12) is not from the ideal chain behavior of semi-flexible chain at moderate length. Therefore, we can conclude that the scaling relation $\langle R_{||} \rangle \sim ND_e^{-1}$ is due to the local stiffness of polymer in the regime $l_p < D_e < xl_p$. Such a local stiffness might result in the significant segment alignment close to the channel walls.^[21]

CONCLUSIONS

The conformational properties of flexible and semi-flexible polymer chains in cylindrical channel are simulated using

off-lattice dynamic Monte Carlo method. The scaling relations between the mean end-to-end distance of polymer along the cylindrical axial direction, $\langle R_{\parallel} \rangle$, and the effective diameter of channel, D_e , are mainly studied. We find different scaling relations for the flexible and semi-flexible polymer chains in the region between the strong confined Odijk regime at very small $D_e \ll l_p$ and weak confined regime at large $D_e \gg R_g$.

For the flexible polymer chain, our results show one scaling relation $\langle R_{\parallel} \rangle \sim ND_e^{-0.7}$ in the classic de Gennes regime $l_p^2/b < D_e < R_g$, which is in agreement with free energy analysis as well as blob theory. As for the semi-flexible polymer chain, we find two scaling relations: $\langle R_x \rangle \sim ND_e^{-1}$ in the transition regime $l_p < D_e < xl_p$ ($x > 1$) and $\langle R_{\parallel} \rangle \sim D_e^{-0.7}$ in the classic de Gennes regime at larger $D_e > xl_p$. The width of the transition regime $(x - 1)l_p$ is dependent on the polymer length N and chain stiffness. Our simulation results show that the scaling relation $\langle R_{\parallel} \rangle \sim ND_e^{-1}$ is probably due to the local stiffness of the polymer in small channels with $l_p < D_e < xl_p$.

We find the classic de Gennes regime of the semi-flexible polymer is different from that of the flexible polymer. For the semi-flexible polymer, the channel size region $D_e > xl_p$ with the scaling relation $\langle R_{\parallel} \rangle \sim D_e^{-0.7}$ is different from that for the flexible polymer ($l_p^2/b < D_e < R_g$). Moreover, the relation between $\langle R_{\parallel} \rangle$ and N is not clear for the semi-flexible polymer.

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