Simulations of Gaussian and Excluded-Volume Chains in Curved Slits

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Abstract. We propose polymer models for Monte Carlo simulation and apply them to a polymer chain confined in a thin box which has both curved and flat sides, and show that either a Gaussian or an excluded-volume chain spends more time in the curved region than in the flat region. The ratio of the probability of finding a chain in the curved region and in flat region increases exponentially with increasing chain length up to a certain length defined by the size of box.

Yaman *et al.* [1] showed that an ideal (Gaussian) polymer confined between cylindrical shells has a lower free energy than one confined between two flat surfaces. The difference is

$$\Delta F \sim -kTN\frac{l^2}{24a^2}, \tag{1}$$

where N, l, and a corresponds to the number of links, the size of the link, and the radius of the inner surface of the shell, respectively. It does not depend on the slit width d. They discussed that polymer chains confined in bilayer membranes reduce the effective bending rigidity of the membranes and might induce spontaneous curvature in the system, e.g. leading to transitions from lamellar to bicontinuous phases. [2]

Their studies of the confinement effects are limited to ideal polymers described by the continous random walk. It is assumed in their analysis that $l \ll d$, $d \ll a$, and $d \ll R_g$ where R_g denotes a typical size (gyration radius) of the chain in free space. Their result is, therefore, valid asymptotically at large N in a small curvature slit. The ideal chain can act as an unperturbed model of a perturbation calculation for the "real" chain in a good solvent characterized by excluded-volume interactions. It is, however, difficult for confined polymers and few publications have addressed the excluded-volume effects. [3]

Our polymer models are off-lattice and consist of $N+1$ beads and N bonds; they are relaxed versions of the random flight model with variable bond lengths. (1) Connectivity: $|r_i - r_{i+1}| \leq 1.0$, where $r_i = (r_{ix}, r_{iy}, r_{iz})$ stands for the position of the i-th bead. (2) Excluded-volume: $|r_i - r_j| \geq 2r_e$, for all i, j, where r_e is the radius of beads. (3) Geometric constraint: the position of beads are in a confining geometry, here a race-track box (Fig. 1). Note that we impose the last condition only on beads, but not on bonds. Thus, we even allow a bond that cuts through the curved wall as long as two beads attached to the bond satisfy the geometric constraint. We consider two models: Model-G which requires (1) and (3), and Model-E which requires (1)–(3). They correspond to the Gaussian chain and the excluded-volume chain respectively.

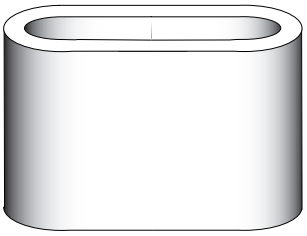

FIGURE 1. Race-track slit: the width of the slit is d.

Our Monte Carlo (MC) algorithm is the following. i) Select a bead at random. ii) Generate a trial jump: $r_i \to r_i + \Delta$. Each component of the jump vector Δ_μ ($\mu = 1, 2, \cdots, n$) is independently determined by the Gaussian distribution with zero mean value and a standard deviation of 0.3 for Model-G and 0.15 for Model-E. The Gaussian distribution is generated by the Box-Muller method. [4] iii) Check if the new position satisfies above mentioned conditions: (1) and (3) for Model-G, (1)–(3) for Model-E; if it does, accept the jump; if not, abandon the jump. iv) Return to i). For a simulation with $N+1$ beads, $N+1$ cycles comprise one MC step.

For Model-E, we use the same race-track geometry as used for Model-G. Note that the width of the race-track $d = 0.5$ is defined based on the center of the beads. When the width is defined based on the surface of the beads, it is $d + 2r_e = 1.0$ and the radius of the inside wall is

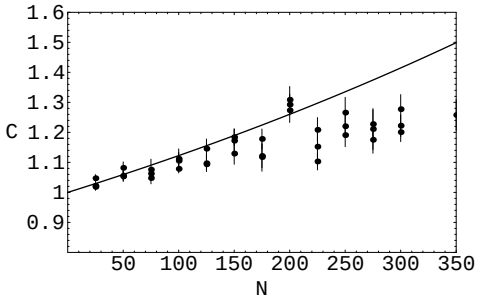

FIGURE 2. Variation of the chain length in Model-I with $d = 0.5, 0.7, 1.0$. The line is drawn according to the theoretical curve with parameters $a = 4.75$, $\langle l^2 \rangle = 0.6$: $C = \exp(N/902.5)$.

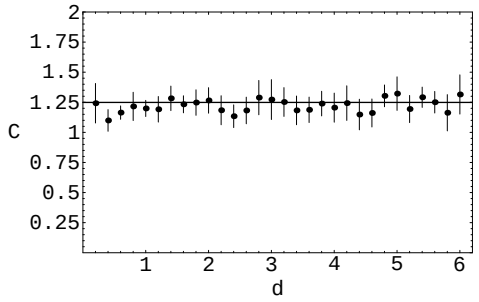

FIGURE 3. Variation of slit width in Model-I with $a = 4.75$. The line indicates $C = 1.249$ which is predicted by the theory.

$a - r_e = 4.5$ where $r_e = 0.25$ is the radius of the beads.

For each model and each polymer length, we carried out 5 runs of simulation with 4×10^8 MC steps after an initial randomized stage (10^6 MC steps). We have calculated the ratio of probability C finding a polymer between in a curved region and in a flat region as a function of chain length N with the formula:

$$C = e^{-\Delta F/kT} = \exp\left(\frac{Nl^2}{24a^2}\right). \qquad (2)$$

In Model-G, our simulation results (Fig. 2) does not depend on d. The chain length dependency fits the analytical formula (Fig. 3) as far as the chain lengths are short. In Model-E, our results (Fig. 4) are also well described by the same formula for short chains. However, they show a deviation when the chain gets longer.

Snap-shots show that shapes of confined chains are elongated compared with the chain in free space. The gyration radius of confined chain with $N+1 = 125 \sim 175$ (for Model-G, $d = 0.5 \sim 1.0$) and with $N+1 = 75$ (for Model-E, $d = 0.5$) is comparable to the section length $L \sim \pi a$. When the size of chains exceed a single section, the probability does not follow Eq. 2. For longer chains, a single curved section cannot accommodate the whole chain. Therefore, deviation from the theoretical curve is

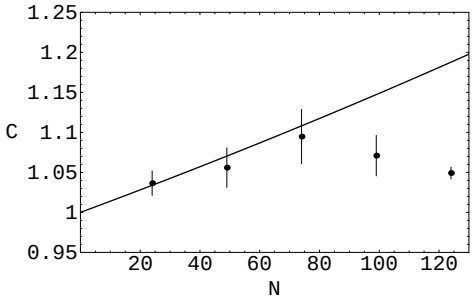

FIGURE 4. Results of Model-E with $d = 0.5$ and $a = 4.75$. The line is drawn according to the theoretical curve for a Gaussian chain with parameters $a = 4.5$, $\langle l^2 \rangle = 0.664$: $C = \exp(N/720.9)$.

consistent with our analysis. The longer Gaussian chains can be squeezed into the curved section, however, the excluded-volume chains can not. The probability ratio C become constant beyond the threshold length for Model-G and reach a maximum at the threshold for Model-E.

We present new polymer models for Monte Carlo simulation for efficient changes of the polymer conformation in confining geometries by the variable bond lengths and the variable jump distances. We have investigated the curvature effect on a polymer confined in a thin box. Our results agree quantitatively with the prediction by the analytical theory up to a certain polymer length determined by the confining geometry. Beyond the length, the effect stays constant for the Gaussian chain and it decreases for the excluded-volume chain. The effect is screened by the excluded-volume interactions for longer chain.

Due to restriction on the scale of confining geometry, our simulations only cover the linear region of C as a function of chain length ($N \ll a^2/l^2$). However, our results may still be useful under present circumstances where there is no experimental data for either ideal or excluded-volume chains and there is no analytical theory for excluded-volume chains.

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