Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Dynamics of polymer chain confined in a periodic cylinder: Molecular dynamics simulation vs Lifson-Jackson formula

Jiaxin Wu, Zhiyong Yang, Xiaoou Cai and Linxi Zhang

S1. The initial equilibrium of system

Figure S1 shows the total potential energy of a single flexible polymer chain confined in a periodic cylinder with L_1=L_2=16 as a function of the iteration steps t'. Here the total potential energy E includes all bond and nonbond energies for polymers. The evolution of the total potential suggests that the simulated system has been equilibrated after $1*10^7$ steps and the point t=0 means that one begins to collect the samples.

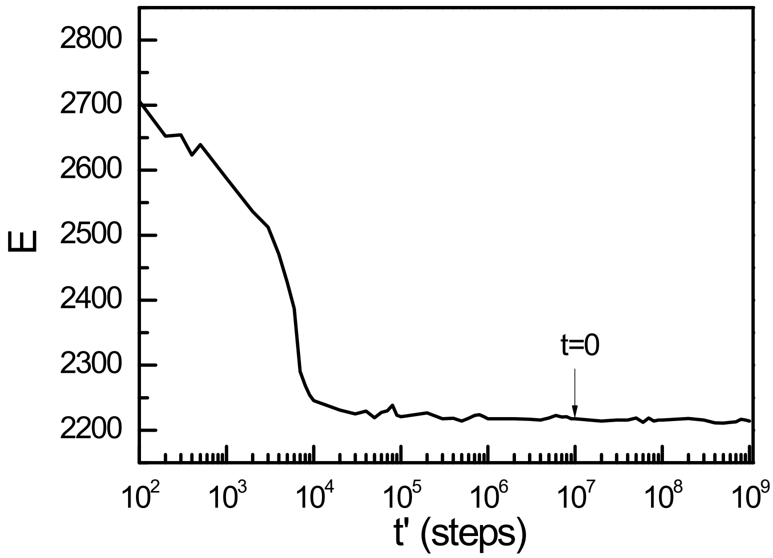

Fig. S1. The total potential energy of the system E as a function of the iteration step t'. t=0 is marked at t'=$1*10^7$ (steps). Here N=100, and L_1=L_2=16.

S2. The simulation box sizes with different periodicities of cylinder L

The size of simulation box relies on the periodicity of cylinder L, and the detailed data for the simulation box of $L_x \times 100 \times 100$ is given in Table S1. Here the cylinder is set periodically in the x-direction.

Table S1. The size of simulation box along the x-direction, L_x, with different periodicities of cylinder L and different chain lengths N.

L	L_x		
	$N \leq 100$	$100 < N \leq 200$	$200 < N \leq 300$
8	96		
16	96		
28	112	140	224
32	96	160	224
36	108	144	216
40	120	160	240
48	96		

S3. The diffusion behavior of a single flexible polymer chain in free space

In order to explore the effects of the confinement size on the conformations and dynamics of polymer chain, we investigate the average size and the diffusion behavior of a single flexible polymer chain in free space and the results are shown in Figs. S2 and S3.

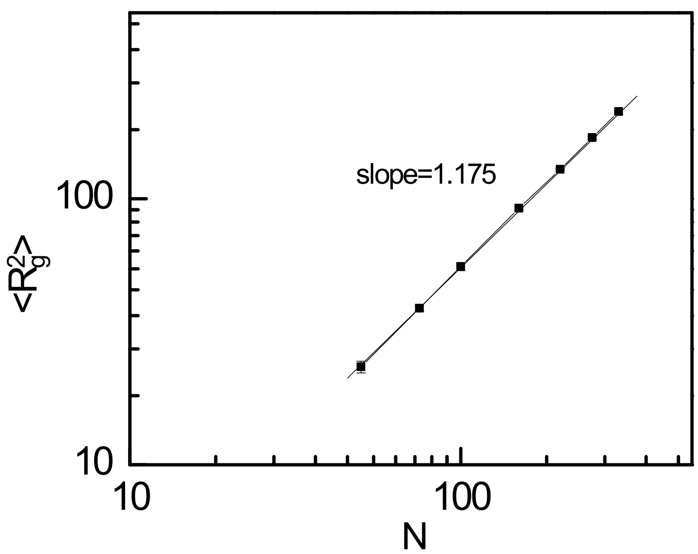

Fig. S2. The mean-square radius of gyration $< R_g^2 >$ of a single flexible polymer chain as a function of chain length N in free space.

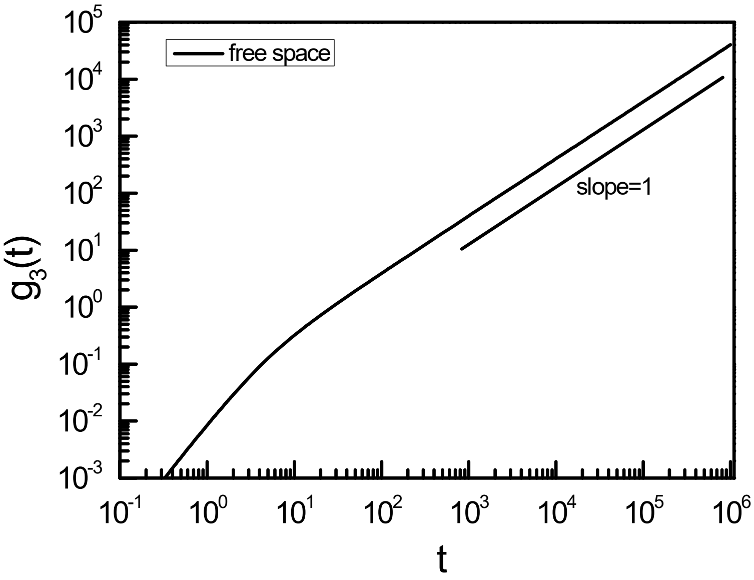

Fig. S3. MSD of the center-of-mass along the x-direction, $g_{3,x}(t)$, of a single flexible polymer chain in free space. Here N=100, and $R_g = \sqrt{<R_g^2>}$ =7.46.

S4. The effects of confinement size d on the dynamics of a single polymer chain confined in an infinite cylinder

We calculate the diffusion coefficient D of a single polymer chain confined in an infinite cylinder with different channel sizes d (i.e., the diameter of channel), and the results are shown in Fig. S4. Although the diffusion coefficients for d=7 and d=10 are approximately equal (D ≈ 0.02), the effects of channel size on diffusion coefficient are obvious for the strong confinement, and the diffusion coefficient D decreases abruptly with the channel size d decreases for d ≤ 6. For example, it decreases from D=0.019 for d=6 to D=0.010 for d=3.

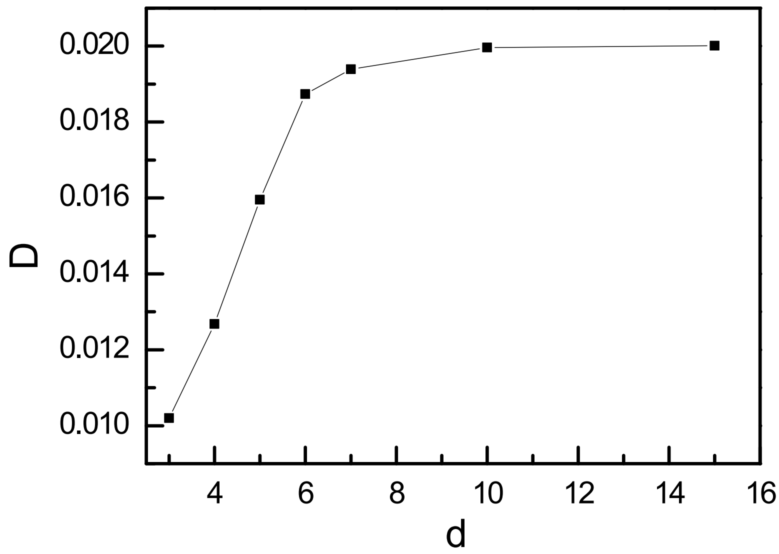

Fig S4. The diffusion coefficient D of a single polymer chain confined in an infinite cylinder as a function of the diameter of infinite cylinder d. Her the diameter of infinite cylinder is uniform and N=100.

S5. The detailed diffusion behavior of a single polymer chain confined in a periodic cylinder under the condition of $L_1 + L_2 = 40$

There are two opposing effects. On the one hand, if L_1 is small, there is not enough space in a cavity for the whole chain. If L_1 is large, the constriction parts of the channel are shorter and the chain does not lose as much entropy if it crosses one. However, these two effects are not symmetric, and the slowest diffusion occurs at $L_1 \neq L_2$. In order to prove this hypothesis, we calculate the diffusion coefficient D with different L_1 of L_1=19, 21, 22, 23, 24, and 25 under the condition of $L_1 + L_2 = 40$, and the results are shown in Figure S5. Actually, the slowest diffusion occurs at L_1=23, not L_1=20, which can prove that these two effects are not symmetric.

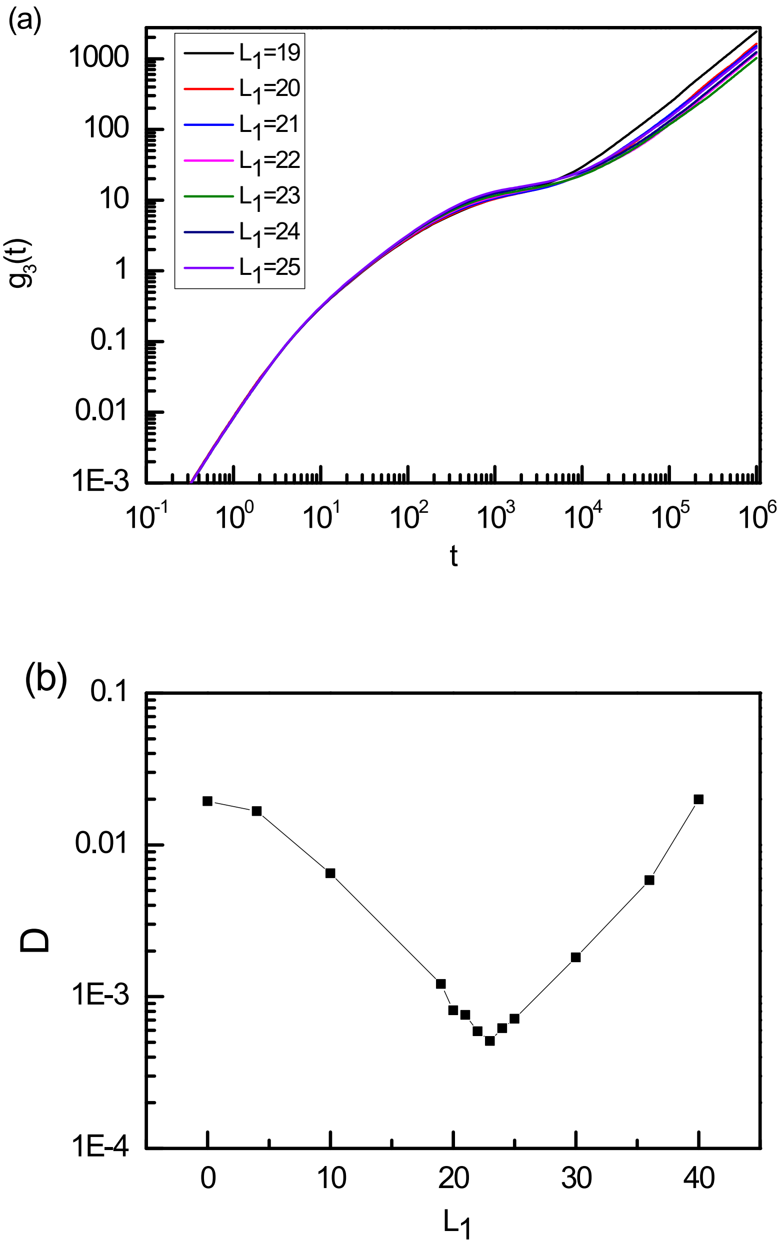

Fig. S5. (a) MSD of the center-of-mass, $g_3(t)$, of a single flexible polymer chain confined in a periodic cylinder with different lengths L_1 of cavity I· (b) Diffusion coefficient D of a single flexible polymer chain confined in a periodic cylinder as a function of length of cavity I, L_1. Here the period length of cylinder keeps a constant of 40, i.e., $L_1 + L_2 = 40$, and N=100.