

## Structure and Dynamics of Dilute Two-Dimensional Ring Polymer Solutions<sup>†</sup>

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Structure and Dynamics of dilute two-dimensional (2D) ring polymer solutions are investigated by using discontinuous molecular dynamics simulations. A ring polymer and solvent molecules are modeled as a tangent-hard disc chain and hard discs, respectively. Some of solvent molecules are confined inside the 2D ring polymer unlike in 2D linear polymer solutions or three-dimensional polymer solutions. The structure and the dynamics of the 2D ring polymers change significantly with the number ( $N_{in}$ ) of such solvent molecules inside the 2D ring polymers. The mean-squared radius of gyration ( $R^2$ ) increases with  $N_{in}$  and scales as  $R \sim N^\nu$  with the scaling exponent  $\nu$  that depends on  $N_{in}$ . When  $N_{in}$  is large enough,  $\nu \approx 1$ , which is consistent with experiments. Meanwhile, for a small  $N_{in} \approx 0.66$  and the 2D ring polymers show unexpected structure. The diffusion coefficient ( $D$ ) and the rotational relaxation time ( $\tau_{rot}$ ) are also sensitive to  $N_{in}$ :  $D$  decreases and  $\tau$  increases sharply with  $N_{in}$ .  $D$  of 2D ring polymers shows a strong size-dependency, i.e.,  $D \sim \ln(L)$ , where  $L$  is the simulation cell dimension. But the rotational diffusion and its relaxation time ( $\tau_{rot}$ ) are not-size dependent. More interestingly, the scaling behavior of  $\tau_{rot}$  also changes with  $N_{in}$ ; for a large  $N_{in}$   $\tau_{rot} \sim N^{2.46}$  but for a small  $N_{in}$   $\tau_{rot} \sim N^{1.43}$ .

**Key Words** : Ring polymer, Molecular dynamics, Two-dimensions, Confinement

### Introduction

Polymers confined on surfaces have drawn a great deal of attention due to their industrial importance since polymer thin films<sup>1-6</sup> were widely used for protective coatings, insulating layers or lubricants. Because the performance of polymer thin films should be determined by the structure and the dynamics of polymers on surfaces, there have been extensive theoretical and experimental studies. While the linear polymers on surface are understood relatively well,<sup>3-6</sup> there are only a few studies on the ring polymers on surfaces.<sup>1,2</sup> Because ring polymers possess an additional topological constraint of ring closure, they should show different self-avoiding walk (SAW) statistics, the structure and the dynamics, which should be, therefore, issues of theoretical interest.<sup>7-17</sup> In this paper, we report extensive molecular simulations to investigate the structure and the dynamics of dilute ring polymer solutions strongly confined on surfaces.

Polymers are almost two-dimensional when polymers are adsorbed strongly on a surface with strong enough attraction between monomers and the surface.<sup>3-6</sup> It was reported that the structure of both DNAs on phospholipid bilayers and polyethylene glycols (PEGs) at solid surface were that of a 2D self-avoiding walk, i.e., the radius of gyration ( $R$ ) scaled with the degree of polymerizations ( $N$ ) as  $R \sim N^\nu$  with a scaling exponent  $\nu = 0.75$  for dilute polymer solutions. Yethiraj<sup>5</sup> performed extensive Monte Carlo simulations of strict 2D linear polymers and found that the scaling expo-

nent  $\nu = 0.75$  still held in two dimensions.

On the other hand, recent experiments<sup>1,2</sup> of circular plasmid DNAs on a mica surface confirmed that there were two structural regimes; the SAW regime with  $\nu = 0.75$  and the rigid regime with  $\nu = 1$ . In strict two dimensions, a ring polymer may divide space into the interior and the exterior of the ring polymer. The solvent molecules inside the ring polymer may not diffuse out readily in case the size of solvent molecules is comparable to that of a monomer. Therefore, solvent molecules inside and outside the ring polymer can be separated (*non-crossing constraint*). This non-crossing constraint as well as the topological constraint are intrinsic features of two dimensional ring polymers and should restrict the phase space where the ring polymers may sample. It is, therefore, expected that the number ( $N_{in}$ ) of solvent molecules inside the ring polymer should influence the structure of ring polymers drastically. There have been, however, few studies on the effect of the non-crossing constraint on the physical behaviors of ring polymers.

Linear polymers confined on surfaces show a variety of dynamic behaviors depending on the type of surfaces. For example, DNAs on phospholipid bilayers follow Rouse dynamics<sup>4</sup> and their lateral diffusion coefficient ( $D$ ) scales with  $N$  as  $D \sim N^{\nu_D}$  with  $\nu_D = -1$ . When PEGs are adsorbed on solid surfaces,<sup>3</sup> however, PEGs undergo reptational behavior with  $\nu_D = -2$ . More interesting is that when polymers are confined on surfaces in a strictly 2D fashion with no degree of freedom in a perpendicular direction,  $D$  is very weakly dependent on  $N$ .<sup>18,19</sup> A few simulation studies reported that the transient diffusion coefficient of 2D polymers obtained from the mean-squared displacements (MSDs) was strongly dependent on the simulation cell size

<sup>†</sup>This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

and the diffusion coefficient could not be determined in strict 2D.<sup>19</sup> On the other hand, the dynamics of ring polymers has been hardly investigated. In this work, therefore, we investigate the rotational and the translational diffusion of dilute 2D ring polymer solutions.

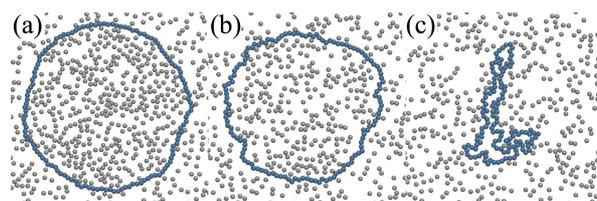
In this paper, we present extensive discontinuous molecular dynamics (DMD) simulations to investigate the dynamics and the structure of dilute 2D polymer solutions. We find from extensive simulations that the value of  $\nu$  depends strongly on  $N_{in}$ ;  $\nu \approx 0.66$  for  $N_{in} = 0$  and  $\nu \approx 1$  for large  $N_{in}$ . This should be purely 2D effect that originates from the non-crossing constraint. The diffusion of a ring polymer slows down as  $N_{in}$  increases. The diffusion coefficient  $D$  is, however, strongly size-dependent as for the 2D linear polymer solutions, i.e.,  $D \sim \log(L)$ , where  $L$  is the simulation cell size. Interesting is that the rotational diffusion is not size-dependent once  $L$  becomes large enough. And the scaling behavior of the rotational relaxation time  $\tau$  also depends on  $N_{in}$ ;  $\tau \sim N^{2.46}$  for large  $N_{in}$  and  $\tau \sim N^{1.43}$  for  $N_{in} = 0$ .

The rest of the paper is organized as follows. The model and simulation methods are described in section II and results are discussed in section III. Conclusions and the summary of the present work are presented in section IV.

### Model and Methods

A dilute two-dimensional ring polymer solution is composed of a 2D ring polymer and many solvent molecules. The 2D ring polymer and solvent molecules are modeled as a tangent hard-disk chain and hard discs, respectively. The diameter of the solvent molecules and monomers is  $\sigma$ , which is the unit length in our simulations. Because any monomer of the ring polymer is covalently bonded to two neighbor monomers, there are no ends for the ring polymer. A string connects chemically bonded hard disks where its interaction is zero if the distance between two hard disks is between 0.95 and 1.05 and infinite otherwise. The degree of polymerizations  $N$  ranges from 32 to 128 in our study. A solvent molecule is modeled as a hard disk of diameter  $\sigma$ . The 2D simulation cell is a square of dimension  $L$  with periodic boundary conditions in all directions. The area fraction of the solvent is  $\phi_{SOL} = N_{SOL} \pi \sigma^2 / 4L^2$ , where  $N_{SOL}$  is the number of solvent molecules.  $\phi_{SOL}$  is fixed as 0.16 and  $L$  ranges from 50 to 200. In our simulations the value of  $\phi_{SOL}$  is fixed because if  $\phi_{SOL}$  were too high above 0.16, the overall dynamics of polymers and solvents would slow down too significantly and the computational time would be beyond our capability. For different values  $\phi_{SOL}$ , the effect of  $N_{in}$  and the strong size-dependency observed in our simulations would remain valid, even if more systematic simulation studies should be desired.

In order to obtain the initial configuration, we insert  $N_{in}$  solvent molecules inside the ring polymer after placing a ring polymer at a random position in the simulation cell. And then we place the rest of the solvent molecules ( $N_{SOL} - N_{in}$ ) at random positions outside the ring polymers. The



**Figure 1.** Simulation snapshots of dilute two dimensional ring polymer solutions of  $N = 128$  with (a)  $N_{in} = N_{in,max}$ , (b) random insertion, and (c)  $N_{in} = 0$ . Blue and grey particles represent the monomers and solvent molecules, respectively.

largest possible number ( $N_{max}$ ) of solvent molecules that one can place inside a ring polymer depends on  $N$ . In our simulations,  $N_{in}$  changes from 0 to  $N_{max}$ . And instead of placing the fixed number ( $N_{in}$ ) of solvent molecules inside the ring polymer, we also insert all the solvent molecules randomly in simulation cells. In this case, the local solvent densities inside and outside the ring polymer are almost identical with  $N_{in} = N_r$ . When inserting a solvent molecule at a random position in the simulation cell, if any overlap occurs between the solvent molecule and pre-existing particles, the random position is discarded and a new random position is tried. This procedure is repeated until the new solvent molecule is inserted successfully.

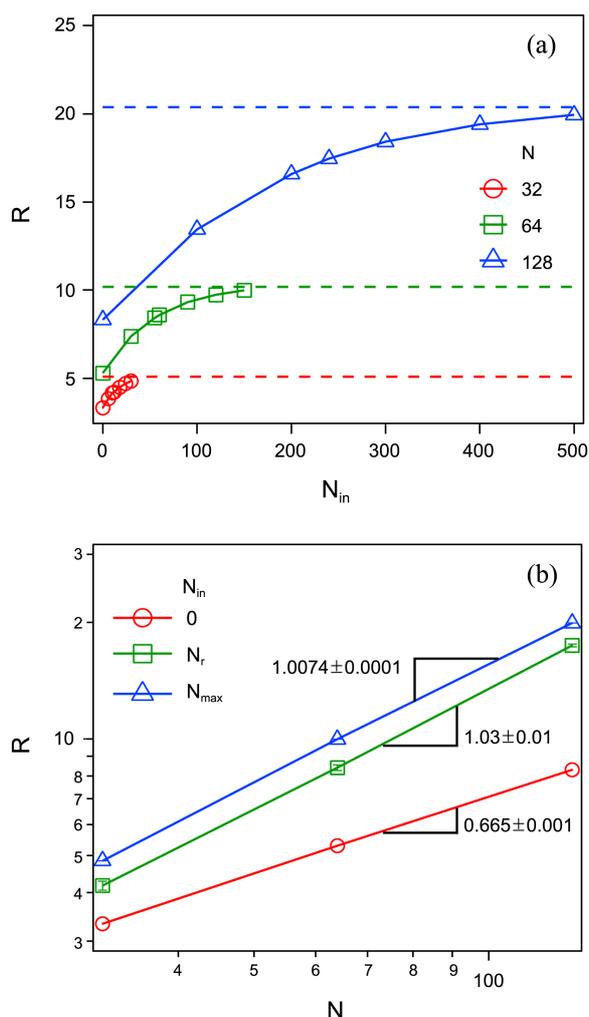
We propagate our system using discontinuous molecular dynamics (DMD) simulations via successive collisions with ballistic motion between collisions because particles interact with each other via a discontinuous potential. For a given set of initial velocities and positions of particles, the most immediate collision pair is sought and the time for the collision is estimated. The system is, then, advanced for the collision time and the velocities of the collision pair are also updated based on the dynamics of an elastic collision. Then the collision pair and the collision for the next collision are evaluated. This procedure is repeated until the system propagates for the desired duration of time. More details on DMD simulation may be found elsewhere.<sup>20-22</sup> In our study, the mass of a monomer is the same as that of a solvent molecule and used as the unit of mass. Temperature  $k_B T$  is set to unity, where  $k_B$  is Boltzmann's constant and  $T$  is the temperature. The unit of time is, then, defined as  $\tau \equiv \sqrt{m \sigma^2 / k_B T}$ . The initial configurations of the systems are equilibrated until each ring polymer diffuses over its average radius of gyration.

Various dynamic and structural properties are calculated including the mean-squared displacements and diffusion coefficients. The mean-squared displacement of the center of mass of a two-dimensional ring polymer is defined as  $\langle R^2(t) \rangle = \langle \{ \mathbf{r}_{COM}(t) - \mathbf{r}_{COM}(t=0) \}^2 \rangle$  where  $\mathbf{r}_{COM}(t)$  denotes the position vector of the center of mass of the ring polymer at time  $t$ . The diffusion coefficient  $D$  is determined from the slope of the mean-squared displacement at long times, i.e.,  $D = \lim_{t \rightarrow \infty} \langle R^2(t) \rangle / 4t$ . Because the end-to-end vector can not be defined for a ring polymer, we monitor the rotational dynamics by calculating the time correlation function  $U(t) = \langle \mathbf{n}_{1M}(t) \mathbf{n}_{1M}(t=0) \rangle$ , of a diameter vector,  $\mathbf{n}_{1M}(t) \equiv | \mathbf{r}_1(t) - \mathbf{r}_M(t) | / | \mathbf{r}_1(t) - \mathbf{r}_M(t) |$ , where  $\mathbf{r}_1(t)$  and  $\mathbf{r}_M(t)$  are

the position vectors of the 1<sup>st</sup> monomer and the Mth ( $= (N+1)/2$ ) monomer. The rotational relaxation time  $\tau_{rot}$  is, then, obtained by fitting  $U(t)$  to  $\exp(-t/\tau_{rot})$  at short times. The average size of the ring polymer is evaluated from the mean-squared radius of gyration,  $R^2 = \langle R_g^2 \rangle = \frac{1}{2N^2} \sum_{j,k=1}^N \langle (\mathbf{r}_j - \mathbf{r}_k)^2 \rangle$ .

## Results and Discussions

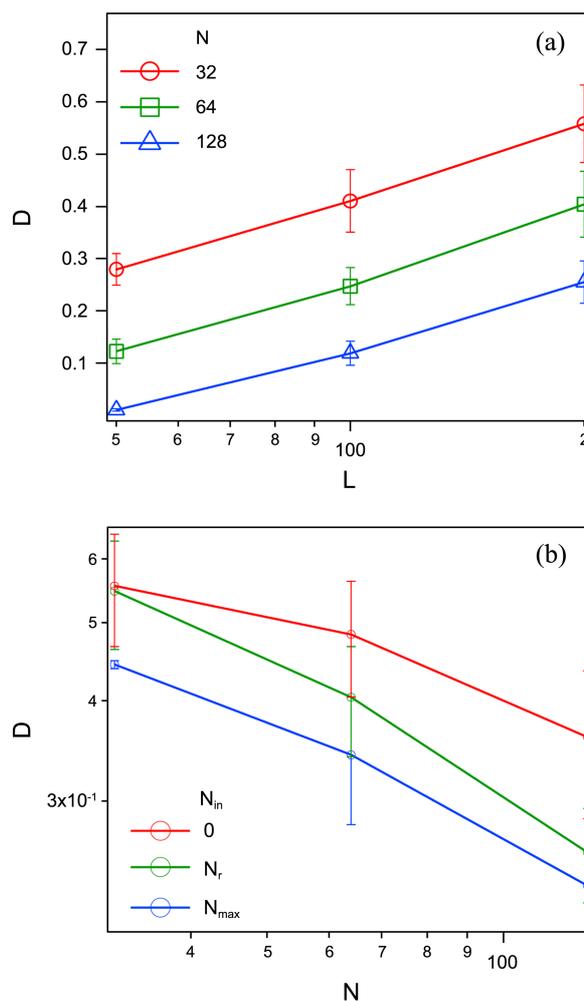
The conformation of a 2D ring polymer changes drastically with how many solvent molecules are confined inside the ring polymer. As one may expect, the size of the ring polymer increases significantly with  $N_{in}$  as depicted in Figure 2(a). Without any solvent inside the ring polymer ( $N_{in} = 0$ ), the ring polymer chains shrink. (Figure 1(c)). The long-dashed lines in the Figure 2(a) indicate the values of squared-radii of gyrations of hypothetically perfect circles for each  $N$ .  $R$  of ring polymers reaches the long-dashed lines as  $N_{in}$  increases implying that  $N_{in}$  used in our simulations are large enough to swell the ring polymer to a maximum extent.



**Figure 2.** Simulation results for  $R$  as a function of (a)  $N_{in}$  and (b)  $N$ . When  $N_{in} = N_{max}$ , the maximum possible number of solvent molecules are inserted inside the ring. For  $N_{in} = N_r$ , the local solvent densities inside and the outside the ring polymer is almost identical.

The size of the ring polymer without any solvent inside it is less than 25% of that of the most swollen ring polymer.

More interesting is that even the scaling behavior changes drastically with  $N_{in}$ . As shown in Figure 2(b), the  $R$  of a ring polymer with  $N_{in} = 0$  scales as  $R \sim N^{0.665}$ . For large enough  $N_{in}$ , however,  $R \sim N$ . It is well established by both theories and simulations that the exponent  $\nu$  of  $R$  of linear polymers at dilute solutions is  $3/4$ . A recent experiment on the circular DNA on a mica surface showed that  $\nu$  of a circular DNA changed from 1 to 0.75 as the circular DNA became larger. Because a short circular DNA was quite stiff, the chain showed a larger value of  $\nu$ . But for a longer circular DNA whose persistence length should be small compared to the circular DNA length, the self-avoiding walk exponent of  $3/4$  was recovered. In our simulations, a ring polymer becomes quite stiff with a large enough number of solvent molecules in it (large  $N_{in}$ ), resulting in  $\nu \approx 1$ . On the other hand, ring polymers with  $N_{in} = 0$  are relatively flexible and  $\nu \approx 0.67$ . But the value of  $N$  used in our simulations is not large enough to test the SAW regime with  $\nu \approx 3/4$ . And in our simulations, only three data points are used to extract  $\nu$ . More simulations with large values of  $N$  would be necessary



**Figure 3.** Simulation results for the transient diffusion coefficients  $D$  obtained from mean-squared displacements at long times as a function of (a)  $L$  and (b)  $N$ .

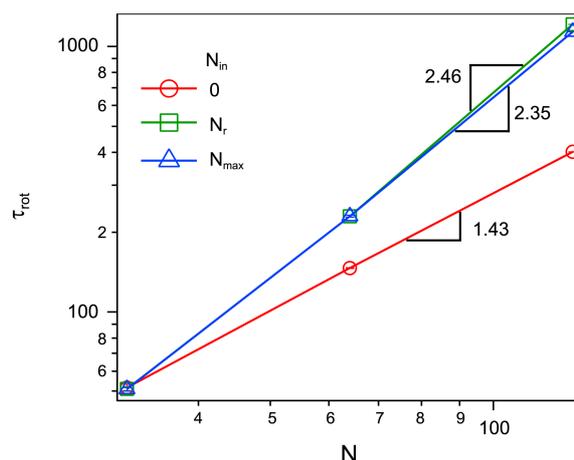
to confirm the other scaling regimes observed in experiments. One caveat is that even though the circular DNA was strongly adsorbed on to the mica surface, a certain part of the circular DNA should be detached from the surface forming multiple loops. In such cases, the direct comparison between our simulation results of strict 2D ring polymers and the experiments would not be valid.

The dynamics of 2D *linear* polymers on a surface shows rich behaviors depending on the interaction between the polymer and the surface. The lateral diffusion coefficient  $D$  of linear DNAs on a lipid bilayer scales with the number ( $N$ ) of base pairs as  $D \sim N^{-1}$  following the Rouse dynamics.<sup>4</sup> Meanwhile, the diffusion of polyethylene glycols (PEGs) at solid surfaces<sup>3</sup> is more strongly dependent on  $N$ , i.e.,  $D \sim N^{-2}$ . For a strictly 2D linear polymer,<sup>18,19</sup>  $D$  scales as  $N^{-1}$  when hydrodynamic interaction is ignored. But with hydrodynamic interaction,  $D$  is not sensitive to  $N$ . The values of  $D$  obtained from molecular simulations are strongly size-dependent and  $D$  increases with the simulation cell size  $L$ , i.e.,  $D \sim \log(L)$ . There has been, however, few simulation studies on the dynamics of 2D ring polymers in dilute solutions.

We obtain the diffusion coefficient  $D$  of 2D ring polymers in dilute solutions from the mean-squared displacements (MSDs). In our simulations, MSDs are all linear to time  $t$  at long times and enter the normal diffusive regime. But,  $D$  is strongly size-dependent in the same way as 2D linear polymers. As depicted in Figure 3(a),  $D \sim \log(L)$  for any value of  $N$ . The strong-size dependency of  $D$  on  $L$  should originate from the long time tail of the velocity autocorrelation function due to hydrodynamic interactions. 2D linear polymers also showed the same strong size-dependency of  $D$ .

The number ( $N_{in}$ ) of solvent molecules confined inside the ring polymer also significantly influences the diffusion of a ring polymer. (Fig. 3(b))  $D$  decreases with  $N_{in}$ , which is not only because the average size ( $R$ ) increases with  $N_{in}$  but also because a ring polymer should accompany the solvent molecules inside it, which would increase the effective mass of the ring polymer. The diffusion coefficients of both a ring and solvent molecules in the ring are the same. And the diffusion coefficient for a given  $L$  does not show a particular scaling behavior. This can be attributed partly to the fact that values of  $N$  in our study are limited to only 128. Further systematical simulation studies would be necessary.

Rotational dynamics of a 2D ring polymer does not display any size-dependency. The time-correlation functions  $U(t)$ 's of diameter vectors do not show any significant deviation from one another for different  $L$ 's. The swollen ring polymers with more solvent molecules in it rotate more slowly. The rotational relaxation time  $\tau_{rot}$  is, therefore, dependent on  $N_{in}$  (Fig. 4). For example, a ring polymer of  $N = 128$  rotates more than two times faster without any solvent molecules in it than with the maximum possible number of solvent molecules. The scaling behavior of  $\tau_{rot}$  is also closely related to  $N_{in}$ . When  $N_{in} = 0$ ,  $\tau_{rot} \sim N^{1.43}$ . But as  $N_{in}$  increases,



**Figure 4.** Simulation results for the rotational relaxation time  $\tau_{rot}$  obtained from the time-correlation functions of diameter vectors as a function of  $N$  for various values of  $N_{in}$ . Dotted lines are fits to the simulation results.

the exponent increases up to 2.46.

## Conclusions and Summary

The structure and the dynamics of a 2D ring polymer in dilute solutions are investigated using DMD simulations. In addition to the intrinsic constraint of ring closure, an additional constraint (non-crossing constraint) is imposed upon the 2D ring polymers; once solvent molecules are inserted inside a ring polymer, they cannot diffuse out the ring polymer. This non-crossing constraint restricts severely the phase space at which the system may sample. Therefore, the structure and the dynamics of a 2D ring polymer should be significantly influenced. Even for the same value of  $N$ , the average size ( $R$ ) increases and its scaling behavior also changes with  $N_{in}$ . In case of dynamics of a 2D ring polymer, both translational and rotational diffusion become slow significantly with  $N_{in}$ . The scaling exponent of the rotational relaxation time  $\tau_{rot}$  increases with  $N_{in}$  up to 2.46.

Our simulation study is limited to a strict 2D ring polymer of moderate size. In order to investigate SAW regime (observed in experiments on circular DNAs on a mica surface), it would be necessary to carry out simulations with a much larger value of  $N$ . And in our future study, we will also simulate the adsorbed ring polymers and will relax the non-crossing constraint in order to further investigate the structure and the dynamics of a ring polymer at surfaces.

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