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Equilibrium size of large ring molecules

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The equilibrium properties of isolated ring molecules were investigated using an off-lattice model with no excluded volume but with dynamics that preserve the topological class. Using an efficient set of long range moves, chains of more than 2000 monomers were studied. Despite the lack of any excluded volume interaction, the size of the chain scaled like that of a self-avoiding walk, as had been previously conjectured. However, this scaling was only seen for chains greater than 500 monomers. [S1063-651X(99)50503-5]

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I. INTRODUCTION

The effects of topology on the equilibrium properties of polymer systems is important both experimentally and theoretically to the understanding of polymeric materials. Many experimental systems, for example as polymer networks, possess nontrivial topology. Furthermore, DNA is often in the form of a ring and possesses a well defined and nontrivial topology. This fact has important biological implications [1,2]. Topological effects arise because a polymer chain cannot cross itself and is therefore confined to a fixed topological class that depends on its initial configuration. However, the effects of topology are, in theory, very hard to understand. The simplest example is that of the ring polymer. Even when it is in the state of a ''trivial'' knot, that is the same topological class as a circle, its statistical properties have not as yet been well understood. This is because there are an infinite number of invariants that characterize a knot and so evaluating, or even writing down, the partition function is a daunting task. Questions about this system, such as how the size of the chain R scales with chain length N, have not been answered with any certainty. The effects of topology on the size of a simple ring have been conjectured to give the same scaling exponent $R \sim N^{\nu}$, as excluded volume [3] chains. It is not clear that ν should be identical to that of the self-avoiding chain. Topological effects may induce effective power law interactions between monomers in the ring. In this Rapid Communication, we wish to analyze how topology alters the fractal dimension of a polymer ring.

To simulate polymers, lattice models have often been employed because in many circumstances they are more efficient and easier to implement than off-lattice models. However, a large class of lattice models with local dynamics has been proven to be strongly nonergodic [4]. Even if an ergodic model is used [5] some of the subtle effects of topology that we wish to examine here can be masked by this kind of model. To avoid segments crossing, which would violate topology, lattice models add in a hard-core repulsion. This makes analysis of the results difficult because this repulsive potential must also be taken into account. The same can be said for many off-lattice models [4,5] that include repulsive potentials between the monomers of the ring. Again this has the problem of masking delicate topological effects making results difficult to interpret.

Therefore it would seem worthwhile to explore an off-lattice model whose interactions are purely topological. The idea is to isolate topological effects to gain some understanding as to how they affect statistical properties.

To achieve this goal we explore topological effects numerically using an efficient off-lattice algorithm which has *no excluded volume*. The chain is a phantom chain, except that it is not allowed to cross itself and therefore can explore only one topological class. As mentioned above, this differs from other work in this area where excluded volume was also present. An efficient long-range algorithm is developed that allows the exploration of rings up to 2048 links. In addition, the chain is more flexible than chains on a cubic lattice, which as we will see is important in light of the results that were obtained.

What was found is rather surprising. We did find that phantom ring polymers confined to the ''trivial knot'' are swollen with respect to phantom linear chains. But even with these very flexible chains, the effect of topology is rather weak, and rings must be longer than 500 links before the scaling exponent ν appears to reach that of a self-avoiding walk (SAW).

II. MODEL

The model is illustrated in Fig. 1. A chain in three dimensions of N links, all of equal length, is constructed so as to have the topology of a simple ring. All configurations are of equal energy; however, moves must not be allowed to alter the topological class. That is, the chain is not allowed to cross itself.

To investigate the dynamics of small chains, moves were chosen that were local, involving rotations of two adjacent links. Moves of this type are illustrated in Fig. 1, where links initially adjacent to A are moved to locations shown by the dashed lines by B. The relaxation time with such moves is slightly greater than N^2, which is prohibitively long for chain lengths in the thousands. Therefore, a long-range algorithm was used instead.

A long-range move is illustrated in the same figure. It is a variation of a pivot algorithm [6]. To construct a new conformation, the algorithm attempts to rotate the chain about some axis. Two points C and D are chosen randomly from the backbone of the chain and the line going through C and D is defined to be the axis of rotation. An angle is chosen randomly between $-90°$ and $90°$ and all chain segments be-

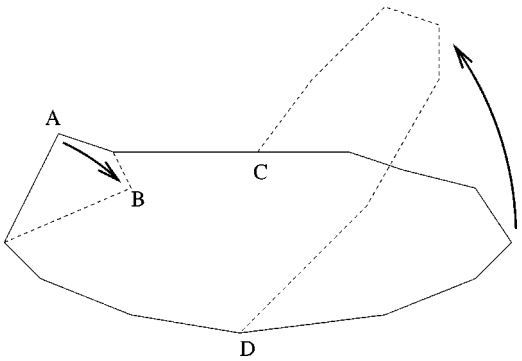

FIG. 1. Moves illustrating the model used. A short range ''kink-jump'' move is depicted on the left-hand side of this figure. A single monomer is moved from position *A* to position *B*. The right-hand side illustrates a long-range move, with the dashed line being the final position of the chain.

tween *C* and *D* are rigidly rotated about this axis. If the ring is found to cross itself as chain segments are being rotated, the move is rejected; otherwise, it is accepted [7]. These long-range moves are repeated millions of times and the chain size *R*, as defined below in Eq. (1), was averaged.

The simulation was tested by starting two rings in a locked configuration and checking to see that they never became unlocked. This test was performed for over 10^8 cycles and always remained locked. The simulation was further tested by taking a long ring of length 512, after it had moved many million cycles, and turning on a repulsive Coulomb potential. It was always found that the ring would swell up into what could clearly be seen as being a circle, in other words a trivial knot. This contrasted with what happened when a deliberately knotted ring was swollen. There the final configuration was not circular.

The simulation was checked by allowing the ring to cross itself by turning off the checking algorithm. In such a case it is easy to show that $R^2=N/4$, when $N\gg 1$. The results found agreed with this value within statistical error. With the crossing constraint enforced, the average *R* was always larger than this value.

III. RESULTS

The chain size *R* defined as

$$R^2\equiv\frac{2}{N}\sum_{i=0}^{N/2-1}|\mathbf{r}_{i+N/2}-\mathbf{r}_i|^2 \tag{1}$$

was examined by averaging over millions of iterations. Here $\mathbf{r}_i$ is the vector position of the ith monomer, and N is the total number of links in the ring.

Figure 2 shows the R^2 as a function of chain length. The best fit to this line gives an exponent of 1.11 ± 0.03. However the best fit for the last two data points at $N=1024$ and $N=2048$ is an exponent of 1.17 close to the result 1.175 found for a SAW in three dimensions [8]. Because this only involves two data points, the up turn is not statistically significant so we now further analyze this possibility by probing the internal structure of the rings.

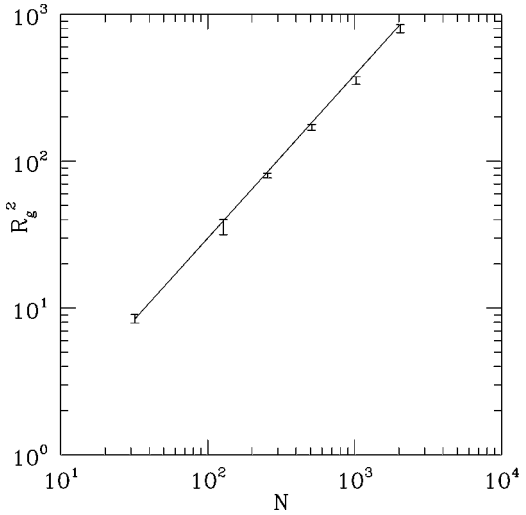

FIG. 2. Average size of a chain defined in Eq. (1) as a function of chain length of rings in the class of a trivial knot. The solid line has a slope of 1.11.

The self-similarity of these rings was examined by means of the correlation function

$$g(s)\equiv\frac{1}{N-s}\sum_{i=0}^{N-s-1}|\mathbf{r}_{i+s}-\mathbf{r}_i|^2. \tag{2}$$

Figure 3 examines how this scales with chain length by writing $g(s)$ in the scaling form

$$g(s)=N^{\nu}f_N(2s/N). \tag{3}$$

The function $f_N(x)$ should become independent of N for large enough N. In Fig. 3, we plot $f_N(x)\equiv g(s)/N^{\nu}$ as a function of $x\equiv 2s/N$. This is done for three different chain lengths, $N=512$, 1024, and 2048. ν was chosen to be 1.17. Note that only the two longest chain lengths overlap. In order to get the 512 link ring to overlap with $N=2048$, a smaller value, $\nu=1.11$, must be chosen. This suggests that the rings of length 512 are not long enough to be in the asymptotic scaling regime.

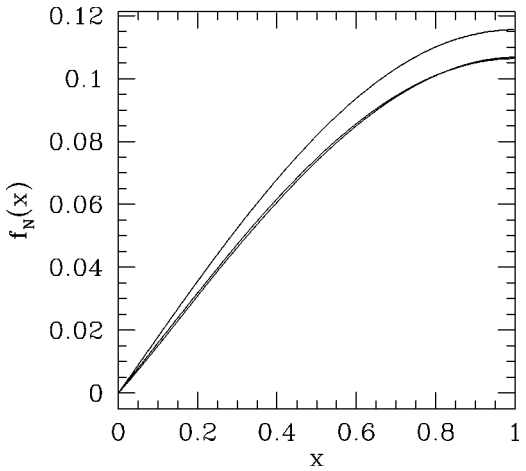

FIG. 3. Scaling function $f_N(x)$ for three ring lengths: 512, 1024, and 2048. Here ν was chosen to be 1.17 and the two larger ring lengths overlap.

IV. DISCUSSION

The results above confirm the prediction that ν for a polymer ring in a trivial knot is swollen compared to an ideal chain. What is surprising is that the length of chain needed to clearly see its asymptotic fractal dimension is in the thousands of links. This contrasts with a self-avoiding walk, where ν can be calculated from chain lengths in the teens to quite high accuracy.

Fairly compelling arguments have been given as to why ν_{ring} for a trivial ring should be greater than or equal to ν_{SAW} for a linear SAW [3]. It is still an open question as to whether ν_{ring} is actually greater than ν_{SAW}. There is no answer to this that is available at present. However, if the ring is trapped between two parallel plates, then this is amenable to a fairly convincing analytical argument. It is argued here that when the separation between the plates is very small, so that the walk is almost two-dimensional, the exponent must be less than or equal to ν for an SAW in two dimensions. This taken with the argument that $\nu_{\mathrm{ring}} \geqslant \nu_{\mathrm{SAW}}$, which carries over to this case also, we can conclude that $\nu_{\mathrm{ring}} = \nu_{\mathrm{SAW}}$.

If the separation between the two walls is much less than the length of a link, then the chain is essentially confined to a two-dimensional $x-y$ plane. However, besides the coordinates of the monomers we also must keep track, in a crossing between two links, of which one lies on top. If we want the ring to preserve the initial topology of a trivial knot, some configurations where the chain crosses itself in the $x-y$ plane must be excluded. Essentially the only configurations that are allowed are those of a flattened trivial knot. Therefore, the phase-space of all configurations are the coordinates in the $x-y$ plane, and the type of crossing of which there are two possibilities.

If in addition to the topological constraint, we introduce a fictitious repulsive potential between links in the chain, it seems highly plausible that this can only increase the average size of such chains. In the limit of complete excluded volume, no crossing is allowed, and this system is identical to the usual self-avoiding ring. This is because complete excluded volume implies that there is no crossing allowed at all, and this by itself enforces the topological constraint. Therefore, the size of a ring without the repulsive potential should be less than or equal to that of a two-dimensional SAW.

In three dimensions the numerical results presented here are consistent with an exponent less than or equal to that of a SAW. However, one cannot exclude the possibility that at even longer chain lengths, a ring becomes more swollen than a linear SAW. Until a better theoretical understanding of knots has been achieved, it is not possible to exclude this possibility.

It is surprising that scaling behavior has not yet reached asymptotic behavior for chains of length 512 as the model we have used allows for the formation of nontrivial knotted chains even for rings of six monomers. However, this work is consistent with enumeration of knot types for random phantom rings [9–12], where the mean number of steps needed to observe a nontrivial knot was of the order of hundreds of steps.

From an experimental viewpoint, the rings analyzed here are large but easily achievable experimentally. A linear chain in good solvent could be synthesized with functional endgroups that chemically bond in good solvent. This should create rings that are predominantly trivial knots. By changing solvent conditions to those of theta solvent for linear chains, one should observe that these rings are still swollen, albeit far less so than a linear chain in good solvent.

Ring polymers in other situations [13] are conjectured to have many interesting properties. An example of this is a melt of rings, and this is the subject of active investigation [14]. It might be useful to apply the model described here to these other systems.

ACKNOWLEDGMENTS

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