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# Osmotic pressure of ring polymer solutions: A Monte Carlo study

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Using the wall theorem, the osmotic pressure of ring polymers in solution has been determined using an off-lattice topology conserving Monte Carlo algorithm. The ring polymers are modeled as freely-jointed chains with point-like beads, i.e., under conditions corresponding to  $\theta$ -conditions for the linear chains. The equation of state is determined. It is furthermore demonstrated that a similar equation of state is found for the corresponding linear chains taking beads of size 0.113 in units of bond length. © 2000 American Institute of Physics. [S0021-9606(00)50548-0]

## INTRODUCTION

Ring polymers have intriguing properties which has led to a continuous stream of publications over the last decades (e.g., Refs. 1–8). Ring polymers differ from their linear counterparts by the topological constraints which force a ring polymer conformation to stay within the topological state of preparation. An unlimited number of different topological states (different knot structures and linkages) are possible. However, the synthesis of ring polymers requires extremely dilute solutions thereby strongly reducing the probability of catenate formation.<sup>9</sup> Moreover, if the synthesis takes place under good solvent conditions, knot formation is also strongly suppressed.<sup>1</sup> Therefore, in this paper we will concentrate on unknotted and unconcatenated ring polymers. In a solution of these molecules, the topological constraint leads to an effective repulsion in addition to ordinary excluded volume effects. We will focus on this additional repulsion and consider a ring polymer solution under conditions corresponding to the  $\theta$ -state of the corresponding linear chain. In such a system any interaction observed is solely due to the topological constraints.

Two ring polymers spaced far apart can take on any pair of single chain conformations. However, once they come closer together they start to severely hinder each other. The number of allowed conformations and thus the conformational entropy decreases leading to a repulsive entropic force of topological origin. This repulsive force leads to an increased osmotic pressure, which has been studied theoretically in some detail.<sup>10,11</sup> Here, the most important quantity is the second virial coefficient, which is directly related to the pair interactions between two rings. To investigate this by computer simulations, we consider a system of rings, unknotted and unconcatenated, confined to a box. We use an off-lattice Monte Carlo sampling algorithm designed to conserve the topological state of the system. The ring polymers are modeled as a freely-jointed bead model with point-like beads (i.e., corresponding to zero excluded volume for the linear counterparts). The osmotic pressure is determined as a function of the concentration using the so-called “wall

theorem.”<sup>12–14</sup> This theorem relates the pressure to the monomer density in the vicinity of a hard (impenetrable) wall. In the past it has been successfully employed for linear chain molecules.<sup>15,16</sup> From the equation of state for our ring polymer system the second virial coefficient, exclusively due to the topological constraints, is determined.

To quantify the strength of the topological constraints in terms of an explicit excluded volume, the system of rings is then compared with the linear counterpart taking finite size beads instead of point-like beads. The radius of the beads is varied until the equation of state coincides with that of the ring polymers.

## MODEL AND SIMULATION TECHNIQUE

The molecules are modeled as a collection of beads in continuous space. These beads are connected by bonds of a fixed length, used as the unit of length. The angle between consecutive bonds is not restricted in any way. If the beads are point-like, we are dealing with the freely-jointed chain model and this will be used to study the effect of topological constraints.

Monte Carlo simulations are used with a simulation algorithm that conserves the topological state. Beads are randomly chosen and moved one at a time. The monomer  $\vec{r}_i$  selected is rotated with a randomly chosen rotation angle about the axis through the connected beads  $\vec{r}_{i-1}, \vec{r}_{i+1}$  to its new position  $\vec{r}'_i$  [Fig. 1(a)]. To assure the conservation of the topological state, we imagine that the bead moves from its original position  $\vec{r}_i$  to its new position  $\vec{r}'_i$  along a straight line and require that during this move the bonds connecting the moving bead to the beads  $\vec{r}_{i-1}$  and  $\vec{r}_{i+1}$  do not cross any of the other bonds in the system [Fig. 1(b)]. If the noncrossing constraint is violated, the move is rejected. For the linear chains with finite size beads, used to quantify the repulsion due to the topological constraints in terms of an explicit excluded volume, extra moves are added for the chain ends. Topological constraints play no role here and moves are only rejected if they lead to overlapping beads.

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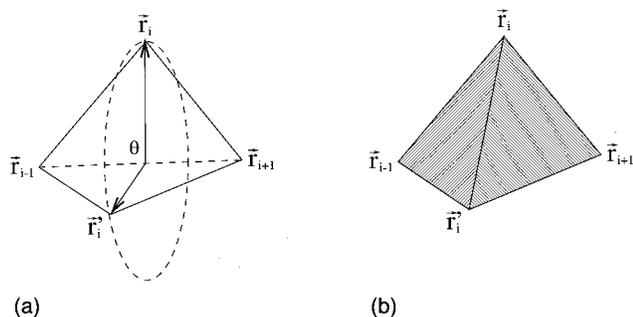


FIG. 1. (a) Illustration of Monte Carlo bead move; (b) noncrossing constraint consists of checking whether any bond in the system crosses any of the two triangles depicted.

## RESULTS AND DISCUSSION

We consider a box of size  $L \times L \times L$  with hard walls. The use of hard walls allows us to calculate the osmotic pressure via the so-called wall theorem,<sup>12–14</sup> which states that the pressure of a system of interacting particles (in units of  $kT$ ) equals the density of the particles at the wall. Applied to our system, this implies that the osmotic pressure  $\pi$  of the ring polymer system is equal to the monomer density  $\rho_{\text{wall}}$  at a hard wall,

$$\frac{\pi}{kT} = \rho_{\text{wall}}. \quad (1)$$

The density profile  $\rho(x)$  has been calculated with walls situated at  $x=0$  and  $x=L$ . To this end, the box was further divided into thin slices and the number of monomers in each slice counted and subsequently averaged over many snapshots. Figure 2 shows a characteristic density profile for 64 16-mers in an  $L=8$  box. The profile shows a strong decrease of the density near the walls due to the large amount of entropy-loss close to the wall. The same figure also shows the density profile for the corresponding phantom rings, i.e., without conservation of topology. The effect of the topology manifests itself clearly in an increased density at the wall.

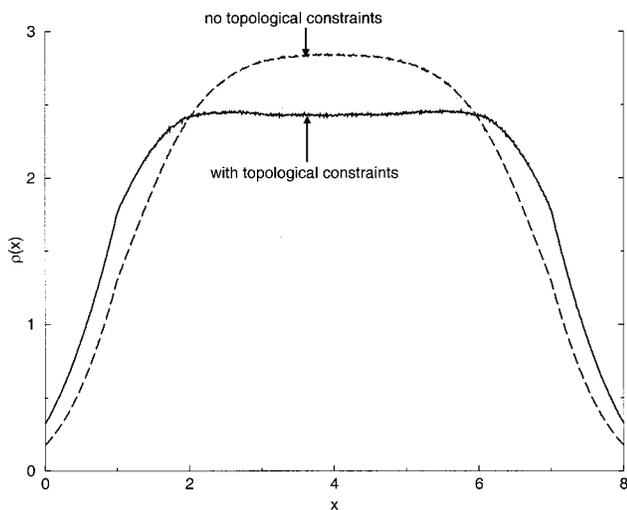


FIG. 2. Density profile of a system consisting of 64 rings of size  $N=16$  in a box of  $L=8$ . For comparison, the density profile for the same system but without topological constraints is also presented.

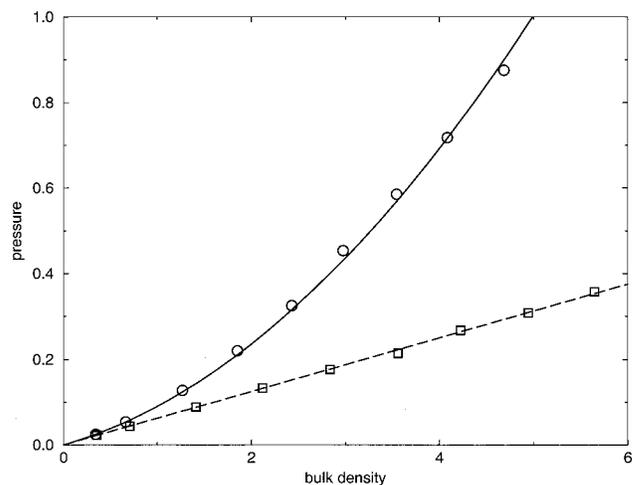


FIG. 3. Pressure–density data (○), together with second virial approximation, Eq. (2) (solid line), for rings of size  $N=16$  in a box of size  $L=8$ . For comparison the pressure–density data for the system without topological constraints is also given (□) together with the ideal gas law (dashed line).

The explanation is straightforward: phantom rings can avoid the reduction in conformational entropy near a hard wall by moving away from it. If topological constraints are present this happens to a lesser extent due to the topological repulsion between different rings. The density is varied by putting different numbers of rings in the box. Each simulation produces a density profile from which two numbers are extracted: the density at the wall and the bulk density. The latter corresponds to the height of the horizontal section of the density curve in the middle of the box. Hence, each simulation gives a point in the pressure–density plane and all simulations combined give the equation of state.

The pressure–density curves have been calculated for rings of various size:  $N=8$ , 16, and 24. Figure 3 shows the result for  $N=16$ . The figure shows that the osmotic pressure of the system with topological constraints is considerably higher than for the phantom rings. In the latter case, the pressure–density curve is nothing but the ideal gas law with every ring polymer replaced by a single particle. The second virial coefficient  $B$  is related to the osmotic pressure in the following way:

$$\frac{\pi}{kT} = \rho_R + B\rho_R^2 + \dots, \quad (2)$$

where  $\rho_R = \rho/N$  is the number of ring molecules per unit volume. A least square fit of Eq. (2) yields  $B=7.1$  for unknotted  $N=16$  ring polymers. For rings of size  $N=8$  and  $N=24$ , the values found are 1.6 and 16.7, respectively.

For comparison, the second virial coefficient was also calculated directly from the topological interaction between two rings. To this end, two rings were prepared in an unknotted and unconcatenated state. An umbrella potential was used to prevent the rings from moving too far away from each other. The topological interaction between the rings is derived from the histogram for the distance between the centers of mass. The histogram is proportional to the probability  $P_0(r)$  of finding a pair of rings placed a distance  $r$  apart in the unknotted and unconcatenated state. The proportionality

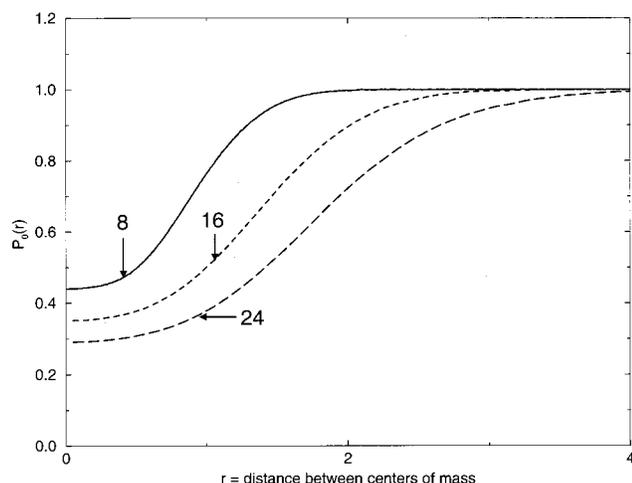


FIG. 4. The probability  $P_0(r)$  that two rings separated by a distance  $r$  are in the unentangled state.

constant is determined from the fact that  $P_0(r)=1$  for  $r$  sufficiently large (Fig. 4). From this, the second virial coefficient is calculated from

$$B = \frac{1}{2} \int (1 - P_0(r)) 4\pi r^2 dr. \quad (3)$$

This alternative route leads to values  $B=1.5$ ,  $6.0$ , and  $14.3$  for  $N=8$ ,  $16$ , and  $24$ , respectively. These values are somewhat smaller than those derived from the osmotic pressure, most likely due to the finite size of the box (i.e., the determination of the bulk density) and the influence of the third virial coefficient. The theoretical analysis presented by Tanaka<sup>11</sup> predicts a much stronger chain length dependence of  $B$ , which may at least be partly due to the relatively small chain lengths employed in our study.

To get an indication of the strength of the repulsion induced by the topological constraint, we next consider the linear counterpart with beads of finite size, a size tuned in such a way that the equations of state coincide. Figure 5 demonstrates that in the case of  $N=16$ , a rather good fit is obtained for linear chains with beads of size  $R=0.113$ . Deviations only start to occur at the highest densities. The same result is found for the other two chain lengths. Hence, as far as the osmotic pressure is concerned the ring polymer system under  $\theta$ -conditions for the linear counterpart closely resembles a system of linear chains with an excluded volume effect corresponding to a bead size of  $R=0.113$ . We can obtain a rough estimate about the temperature distance to the  $\theta$ -temperature of the latter system. To this end we consider a freely-jointed linear chain model with beads of size  $R=0.5$  (in units of bond length). The excluded volume of such a system is approximately equal to

$$V_{\text{excl}} \cong \frac{2}{3} \pi (2R)^3 (1 - 2\chi). \quad (4)$$

Here  $\chi$  is the Flory–Huggins parameter, which usually is positive thereby reducing the excluded volume effect. An

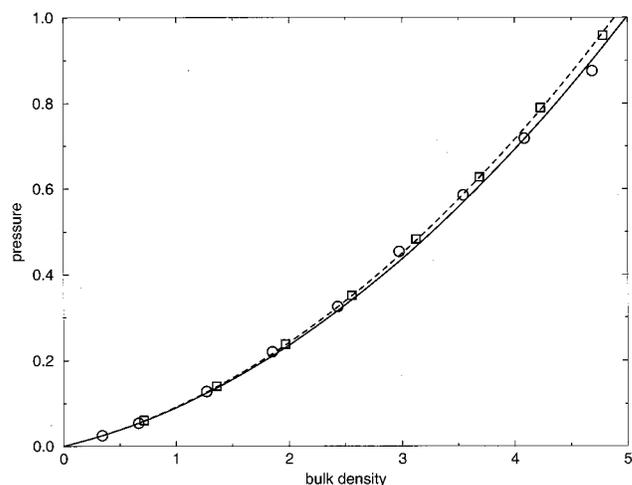


FIG. 5. Pressure–density curve (O) of rings with topological constraints (but without excluded volume) compared to the pressure–density curve (□) of linear chains with excluded volume corresponding to beads of size  $R=0.113$ .

effective bead size of  $R=0.113$  would correspond in this picture to a value of  $\chi=0.494$ .  $\theta$ -conditions correspond to  $\chi=0.5$ . In order to get some feeling for the corresponding temperature difference we use the temperature dependence for the  $\chi$ -parameter of the polystyrene/cyclohexane system as given in Ref. 17,

$$\chi = \frac{64}{T} + 0.29. \quad (5)$$

For this particular parametrization  $\chi=0.494$  corresponds to  $T=313.7$  K and  $\chi=0.5$  to  $T=304.8$  K. In this picture an effective excluded volume of  $R=0.113$  corresponds to a linear polymer system roughly 9 K above its  $\theta$ -conditions. In the case of polystyrene and cyclohexane, the literature value for the  $\theta$ -temperature of ring polystyrene in cyclohexane is 301 K compared to 308 K for linear polystyrene.<sup>9</sup> Of course, the estimates presented should not be taken too seriously, however, the order of magnitude agreement is gratifying.

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