

Osmotic pressure of compressed lattice knots

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(Received 22 February 2019; published 8 July 2019)

A numerical simulation shows that the osmotic pressure of compressed lattice knots is a function of knot type, and so of entanglements. The osmotic pressure for the unknot goes through a negative minimum at low concentrations, but in the case of nontrivial knot types 3_1 and 4_1 it is negative for low concentrations. At high concentrations the osmotic pressure is divergent, as predicted by Flory-Huggins theory. The numerical results show that each knot type has an equilibrium length where the osmotic pressure for monomers to migrate into and out of the lattice knot is zero. Moreover, the lattice unknot is found to have two equilibria, one unstable, and one stable, whereas the lattice knots of type 3_1 and 4_1 have one stable equilibrium each.

DOI: [10.1103/PhysRevE.100.012501](https://doi.org/10.1103/PhysRevE.100.012501)**I. INTRODUCTION**

Confinement of a biopolymer (e.g., in an organel in a living cell) causes an increase in knotting [1] and this increases the level of self-entanglements in the backbone of the polymer [2]. It is known that entanglements have an effect on the physical properties of biopolymers such as DNA [3]. Topological entanglement (knotting and linking) also changes the movement of DNA, for example in the ejection of DNA from a viral capsid [4] or the speed of electrophoretic migration of polymers [5–7].

In this paper a model of a confined and self-entangled ring polymer is examined. A particularly simple model is to place a random circular string [8–11] in a box (see Fig. 1). Conformational entropy of the string is reduced by the confining environment of the box and entanglements can be modeled and controlled by fixing the knot type of the string. The entropy of the confined string can be quantified by placing it in a lattice. If it is self-avoiding, then it is a closed self-avoiding walk [11–13] and this is a lattice model of a ring polymer.

While the model in Fig. 1 is interesting from a purely theoretical perspective, it can also be seen as a very simplified model giving a qualitative understanding of the role of entanglement in the properties of random stringlike objects such as DNA and other biopolymers. DNA is a double helix linear polymer normally compressed and compacted in small volumes [14]. Enzymes unwind and release segments of DNA to mediate cellular processes. These released segments have increased conformational degrees of freedom while also being entangled and connected to and confined by other structures in the cell. The entanglements and confining environment reduce the conformational entropy of these segments. Such segments are also subject to random mutations by random events, which may cause deletion or insertion of base pairs (or even sequences of base pairs) in the genome [15–17]. This changes the length of the segments of DNA. The tendency to gain or reduce the length of the DNA segment can be modeled as an osmotic pressure of base pairs in the segment. In another situation, but also involving DNA, the length of segments of DNA are changed by intercalating drugs [18]. *In vitro* these

drugs are in equilibrium in a solvent or bound to the DNA backbone, and so the model in Fig. 1 can similarly be seen as a simplified model of the osmotic pressure of intercalating drugs bound to the DNA backbone.

II. COMPRESSED LATTICE KNOTS

A closed self-avoiding walk is a lattice polygon [19–21]. Lattice polygons are knotted asymptotically with probability one [22,23]. A lattice polygon with fixed knot type is a lattice knot [24,25]. It is known that the entropy of a lattice knot is a function of its knot type [26,27]. Tight lattice knots [24] are minimal length lattice knots [28–30]. The compressibility of tight lattice knots is known to be a function of knot type [31,32].

In Fig. 2 the model in Fig. 1 is quantified by a placing and compressing a lattice knot in a cubical box (this is a lattice version with self-avoidance of the model in Ref. [33]). The entropy of the compressed lattice knot has contributions from translational degrees of freedom (if it is small compared to the side length of the box), from topological constraints (due to entanglements, which depend on the knot type), and from conformational degrees of freedom. In this paper compressed lattice knots of three knot types [34,35], namely, the unknot (0_1), the trefoil (3_1), and the figure eight knot (4_1) will be considered; see Fig. 3.

A cube in the lattice of side-length $L-1$ has volume $V = L^3$ and side length L . The maximum length of a lattice knot confined to a cube of side length L is L^3 if L is even, and L^3-1 if L is odd. The lattice unknot has minimal length 4 and there are $3L(L-1)^2$ ways it can be placed in the cube. The lattice trefoil knot 3_1 can be tied with 24 steps in the cubic lattice [25], and there are 3328 conformations distinct under translations in the cubic lattice [36]. None of these tight lattice trefoils can be realised in a cube of side length 3, but a numerical simulation detected 4168 distinct placements of 3304 tight lattice trefoils in a cube of side length 4, and 30104 distinct placements of tight lattice trefoils in a cube of side length 5. Similarly, a tight lattice figure eight knot 4_1 has minimal length 30 in the cubic lattice [36] and there are 3648

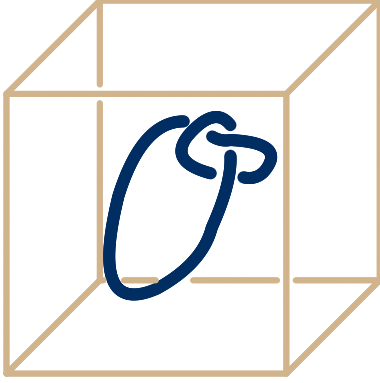


FIG. 1. A model of a knotted ring polymer in a cavity. Contributions to the entropy are due to translational degrees of freedom, topological constraints due to the knot, and conformational degrees of freedom.

conformations distinct under translations in the cubic lattice. A computer count shows that none of these can be realized in a cube of side length 3, but there are 864 distinct placements of tight lattice figure eight knots in a cube of side length 4, and 18048 distinct placements in a cube of side length 5.

III. FREE ENERGY AND OSMOTIC PRESSURE

Denote the number of distinct placements of lattice knots of length n , of knot type K , confined in a cube of side length L , by $p_{n,L}(K)$. Then, for example, $p_{24,3}(3_1) = 0$ and $p_{24,4}(3_1) = 4168$. Approximate enumeration of $p_{n,L}(K)$ can be done by using the GAS algorithm [37] implemented with BFACF moves [38,39]. See Ref. [40] for details.

The concentration of vertices in a lattice knot in a cube of side length L is $\phi = \frac{n}{V}$ where $V = L^3$. The free energy at concentration ϕ of lattice knots of type K is

$$F_{\text{tot}}(\phi; K) = -\log p_{n,L}(K), \tag{1}$$

where $n = \phi V$. The free energy per unit volume is $F_L(\phi; K) = \frac{1}{V} F_{\text{tot}}(\phi; K)$ and this is plotted in Fig. 4 for $2 \leq L \leq 15$ and for $K = 0_1$ (the unknot) against the monomer concentration ϕ . The shape of these curves is consistent with prediction of Flory-Huggins theory [41].

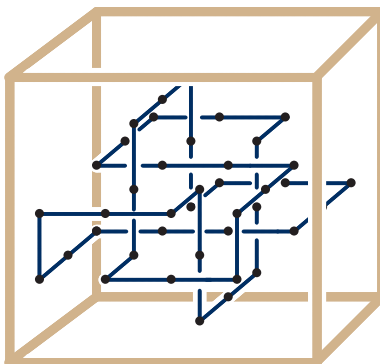


FIG. 2. A lattice knot in a cubical cavity.

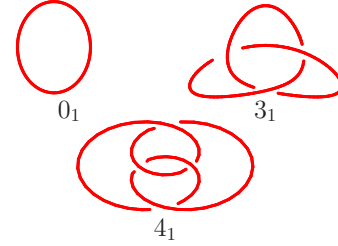


FIG. 3. The unknot 0_1 , the trefoil knot 3_1 and the figure eight knot 4_1 [34,35].

The osmotic pressure $\Pi(\phi; K)$ of compressed lattice knots is given by

$$\Pi(\phi; K) = -\frac{d}{dV} F_{\text{tot}}(\phi; K). \tag{2}$$

Changing variables to ϕ shows that

$$\Pi(\phi; K) = \phi^2 \frac{d}{d\phi} \left(\frac{1}{\phi} F_L(\phi; K) \right) \tag{3}$$

in terms of the free energy per unit volume. This can be computed from the data in Fig. 4 by taking a numerical derivative. Using a central second-order numerical approximation to the derivative gives Fig. 5. This appears to be consistent with the predicted Flory-Huggins osmotic pressure: $\Pi(\phi; 0_1)$ is increasing and sharply diverges as $\phi \rightarrow 1^-$. Closer examination of Fig. 5 shows that $\Pi(\phi; 0_1)$ is not monotone but is decreasing a low concentrations and negative and not monotonic on an interval of low concentrations; see Fig. 6.

At negative osmotic pressure the lattice unknot will add length. Similarly, at positive osmotic pressure the lattice unknot will shed length and become smaller. The pressure curves in Fig. 6 are functions of L and each has two zeros at ϕ_0 and ϕ_m . At concentrations $\phi < \phi_0$ the lattice unknot will evaporate, and when $\phi_0 < \phi < \phi_m$ it will add length until the concentration is ϕ_m (which is a stable fixed point). It will also shed length if $\phi > \phi_m$ until the concentration is ϕ_m .

Lattice polygons of length n has linear size $O(n^\nu)$ where $\nu \approx \frac{3}{5}$ is the metric exponent in three dimensions [12] (a more accurate estimate is $\nu \approx 0.587597(7)$ [42]). Effects of the confining cube will become important when $n^\nu \sim L$. The osmotic pressure should vanish at this point; the result is that $\phi_m \sim L^{1/\nu} / L^3 = L^{1/\nu-3}$. As $\phi \rightarrow 0^+$, $\Pi(\phi; K) \sim L^{-3}$. Using the Flory value for ν and then plotting $\Pi(\phi; K) L^3$ as a function of $\phi L^{3-1/\nu} \approx \phi L^{4/3}$ should collapse the data in Fig. 6. This is shown in Fig. 7, although there are still

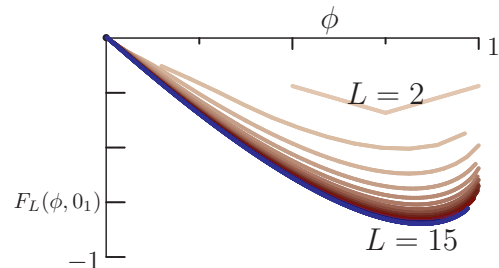


FIG. 4. The free energy per unit volume for unknotted lattice knots, for $2 \leq L \leq 15$.

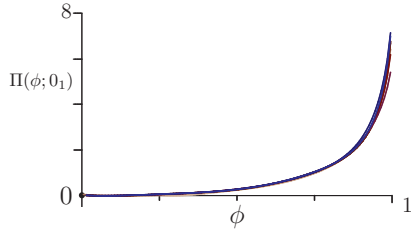


FIG. 5. The calculated osmotic pressure of compressed lattice unknots. The data are for $2 \leq L \leq 15$.

finite-size corrections. Extrapolating the zeros of the curves in Fig. 7 gives $\phi_0 \simeq 0.149 L^{-4/3}$, $\phi_m \simeq 0.286 L^{-4/3}$. Since the osmotic pressure vanishes at these concentrations the equilibrium lengths at which the osmotic pressure vanishes are $n_0 \simeq 0.149 L^{5/3}$ and $n_m \simeq 0.286 L^{5/3}$. The osmotic pressure of the unknot goes through a minimum at $\phi_c \simeq 0.209 L^{-4/3}$.

The osmotic pressures of compressed lattice knots at low concentration and of knot types 3_1 and 4_1 are plotted in Fig. 8. Here the osmotic pressures are monotone increasing with concentration ϕ , passing through zero at a critical concentration ϕ_0 . Rescaling the data in the same way as in Fig. 7 gives Figs. 9 and 10. This shows that for 3_1 , $\phi_0 L^{4/3} \simeq 3.94 L^{-4/3}$, and for 4_1 , $\phi_0 L^{4/3} \simeq 4.48 L^{-4/3}$. For $\phi < \phi_0$ the osmotic pressure is negative and the lattice knot will grow to an equilibrium length $n_0 \simeq 3.94 L^{5/3}$ for 3_1 and $n_0 \simeq 4.48 L^{5/3}$ for 4_1 .

IV. CONCLUSION

In this letter a numerical simulation of compressed lattice knots as a model of an entangled ring polymer show that the osmotic pressure is a function of knot type. Since the level of entanglements is a function of knot type, these results support the notion that the properties of confined biopolymers, such as DNA, is a function of the level of entanglement if the biopolymer is confined or compressed in a narrow space, or adsorbed on a membrane. Adsorption of the knotted polymer on the surface of a membrane was analyzed in the lattice in Ref. [43]. If the polymer can relax freely after adsorption, then the knot localizes and its effects disappear as the length of the polymer increases [44,45]. On the other hand, the adsorbed polymer should have properties of projected three-dimensional polymers; experimental evidence of this was given in Ref. [44].

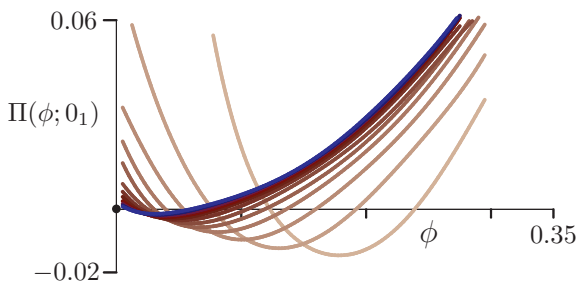


FIG. 6. The osmotic pressure of compressed lattice unknots at low concentration for $3 \leq L \leq 15$.

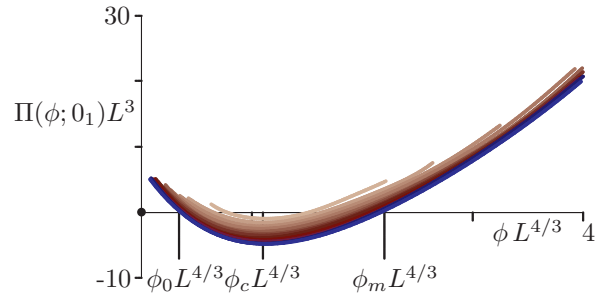


FIG. 7. Rescaled osmotic pressures for the unknot 0_1 , plotted as a function of $\phi L^{4/3}$. The data are for $3 \leq L \leq 15$.

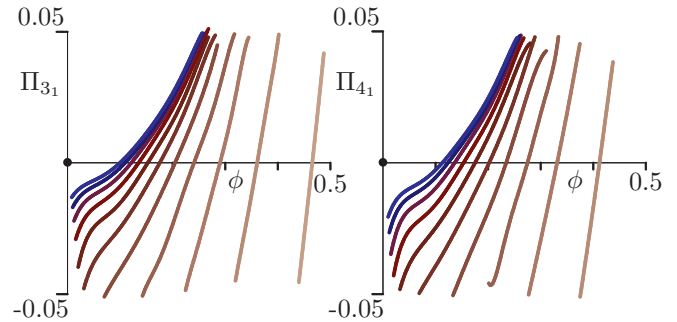


FIG. 8. The osmotic pressure $\Pi_{3_1} \equiv \Pi(\phi; 3_1)$ of the trefoil knot, and $\Pi_{4_1} \equiv \Pi(\phi; 4_1)$ of the figure eight knot plotted against the concentration ϕ for $0 \leq \phi \leq 0.5$.

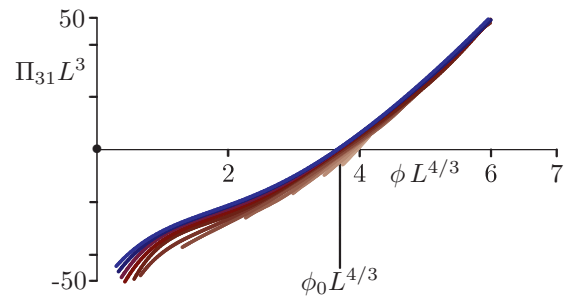


FIG. 9. Rescaled osmotic pressures $\Pi_{3_1} \equiv \Pi(\phi; 3_1)$ for lattice knots of type 3_1 (trefoil). The data are taken from the left panel in Fig. 8 for $4 \leq L \leq 15$.

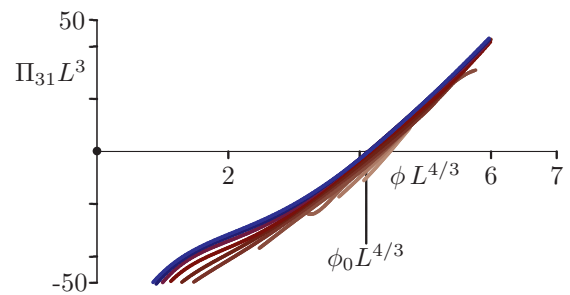


FIG. 10. Rescaled osmotic pressures $\Pi_{4_1} \equiv \Pi(\phi; 4_1)$ for lattice knots of type 4_1 (figure eight knot). The data are taken from the right panel in Fig. 8 for $4 \leq L \leq 15$.

The numerical data in this paper show that the rescaled osmotic pressure vanishes at a critical concentrations, as shown in Figs. 7, 9, and 10, and that these critical concentrations are functions of knot types. In the case of the unknot there are two critical concentrations where the osmotic pressure vanishes. At these concentrations the lattice unknot has an equilibrium length, but at the lower critical concentration this is unstable, and the unknot will tend to grow or evaporate. At the higher critical concentration the equilibrium length is stable. The

situation is not the same for the trefoil and figure eight knot types. In these cases there is one stable equilibrium at a critical concentration, which is dependent on knot type.

ACKNOWLEDGMENTS

E.J.J.v.R. acknowledges support from NSERC(Canada) in the form of Discovery Grant No. RGPIN-2014-04731.

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