Uncrossability of polymer chains in a melt gives rise to a restricted transverse motion of chains, which is represented by a confining "tube". Ultimately, the tube must be of topological origin. We propose two definitions of the tube diameter or entanglement length ($N_e$) in terms of the properties of topologically equilibrated melts of rings: (1) the probability of a ring in such a melt being unknotted is a constant for a ring of length $N_e$; (2) the topological entropy per entanglement strand is $3/2k_B$ for sufficiently long rings. To test these ideas, we simulated a coarse-grained model for polymer rings under aperiodic, 1D and 2D periodic boundary conditions, with molecular rebridging moves to equilibrate the topological states. We then implemented an efficient algorithm for computing the Jones polynomial, in order to identify the topological states. Our purely topological estimates of $N_e$ are quite consistent with previous values based on heuristic chain-shrinking methods.

1 Introduction

Polymer motions in entangled dense melts or solutions are severely constrained by the uncrossability of surrounding molecules. Effectively, polymers may be thought of as being confined inside a tube-like region, freely changing configurations by moving along the tube, but confined in the two transverse directions. The tube diameter $a$ represents the effective width of the confinement. The tube diameter and the monomer friction factor are the two key parameters in the modern theory of polymer rheology, which has successfully explained the diverse viscoelastic properties of polymer materials.

The tube diameter $a$ is a material property, dependent on chain structures at short length scale (chain stiffness, monomer bulkiness, concentration) but not on molecular architectures (long branches, cross-linking). Correspondingly, the entanglement length $N_e$ is defined as the arc length of a chain with mean-square end-to-end distance equal to $a$ ($N_e = (ab)^2$, $b$ being the statistical segment length).

In practice, $N_e$ and $a$ are determined from experiments by comparing measured mechanical responses with rheological model predictions. Most simply, the plateau modulus $G_N$ is proportional to the number density of entanglement strands, i.e., $G_N = (4/5)k_BT(N_e^c)$, where $v$ is the monomer volume. Using this relation, the entanglement length can be inferred.

Significant progress has been made towards practical predictions of the tube diameter for a given polymer structure. On a phenomenological level, the Lin-Noolandi (LN) ansatz states that an entanglement results when sufficient number of chain segments cohabit the same volume. This assertion leads to a simple result: the tube diameter is proportional to the packing length $p$, defined as the ratio of the displaced volume of a chain $V_p$ and its square end-to-end distance $R_e^2$. Both $V_p$ and $R_e^2$ scale linearly with chain length in the melt, hence $p$ is a material property with dimension of length.

The LN relation gives a good account of the dependence of $N_e$ on local chain structures, as shown by Fetters et al., who analyzed extensive data on plateau modulus and chain dimension. Thus in principle, molecular dynamics simulation can be used to determine the purely geometrical properties $V_p$ and $R_e^2$ for a given polymer chemistry, with the LN relation predicting a value for the tube diameter. Indeed, the simulated chains need not be well entangled, but only long enough that their dimensions can be extrapolated to the long-chain limit.

Two heuristic methods to "see" the tube in simulations have been developed: direct visualization of time-averaged chain trajectories in MD simulations of entangled melts, and the chain contraction algorithm and its variants. The chain-shrinking methods fix the chain ends and shrink the chain backbones until the chain paths become a sequence of straight segments between pairwise uncrossability constraints. This is a destructive way of visualizing tube and measuring the entanglement length. Nonetheless, it has yielded good predictions for the entanglement length as a function of microscopic material parameters, by interpreting the average length of the straight segments as the tube diameter.

In contrast, time-averaged chain trajectories result in a smooth curve for the primitive path (centerline of the tube occupied by the chain); this approach suggests a tube with a persistence length and a harmonic confining potential, not necessarily defined by a discrete sequence of pairwise contacts.

Despite these advances, our understanding of the origin of the tube is incomplete. The physical origin of the tube is the uncrossability of chains, which is a topological constraint, yet no...
explicit connection of the tube to topology has been given for flexible polymers.

Our goal is to establish a direct connection between the entanglement length and the statistics of topologically distinct states in an unperturbed melt. By “topologically distinct”, we mean that one state cannot be deformed into another without allowing molecules to cross. The number of topological states \( \Omega \) should depend on the entanglement length \( N_e \), which may be interpreted as the average number of segments required to create an additional topological constraint with surrounding molecules.

In particular, we shall show that the topological entropy in \( \Omega \) for sufficiently long chains is equal to \( 3k_B/2 \) per entanglement length. To test this relation, we simulate topologically equilibrated entangled ring polymers under both aperiodic and periodic boundary conditions (section 3). The topological states are changed by implementing various ring rebridging moves (section 3.1). We accumulate statistics for the frequency of their topological states are well defined; we use periodic boundary conditions in an effort to reduce the finite-size effects of closed system boundaries, across which chains cannot entangle. The main results are discussed in section 5, and summarized in section 6.

2 Entanglement length and knot statistics

In this work, we study ring polymers instead of linear chains. Rings offer several important advantages for studying entanglement effects. In a melt of rings, the topological state is well defined, entanglements are permanent unless the chains are explicitly allowed to cross, and there are no chain end effects. Because entanglement is a local phenomenon on the scale of the tube diameter, a melt of sufficiently long topologically equilibrated rings should be a suitable proxy for an entangled linear melt.

The topological states of a melt of rings are best visualized as knots formed by the primitive paths of the chains. For example, three simple knots that can be made out of a single loop are shown in Fig. 1: the first is a trivial loop or unknot; the second is the simplest nontrivial knot, a trefoil; the third is a figure eight or Savoy knot (widely used in sailing and rock climbing). The labels \( 0_1 \), \( 3_1 \) and \( 4_1 \) are standard names given to these knots: the first number is the crossing number, the minimum number of crossings needed to represent or “draw” the knot, which measures approximately the complexity of knots; the subscript is ordinal number, indexing all possible knots with the same crossing number.

These three examples are all prime knots, which cannot be formed by joining simpler knots. The examples in Fig. 1 exhaust all possible knots with minimum crossing numbers less than five (ignoring the distinction between a knot and its mirror images). The number of knots grows exponentially rapidly with crossing number. A catalog of all prime knots up to 16 crossings is available, with many topological properties and invariants tabulated.

Studies of polymer knots have been pioneered by Frisch and Wasserman,\(^\text{15}\) Delbruck,\(^\text{16}\) and Frank-Kamenetskii et al.\(^\text{17}\) and have expanded significantly in recent years (see ref. 18 for a timely review). Recent studies include efforts to relate the contribution of knotted strands to the elastic modulus in networks using the Gaussian winding number,\(^\text{19}\) and investigations of the untying dynamics of a knotted trefoil.\(^\text{20}\) One quantity of particular interest has been the unknot probability, i.e., the probability that a ring configuration is topologically equivalent to an unknot. The dependence of unknot probability on ring length has been studied in various systems, including self-avoiding random walks in free space, in solutions, and lattice polymers (SC, BCC and FCC). It was found that the unknot probability drops exponentially with ring length, with a characteristic length depending on local chain properties.

Relatively few studies of knots in dense polymer melt have been carried out, perhaps because of the difficulty in preparing suitably equilibrated configurations.\(^\text{21-22}\) Also, previous work on polymer knots have either studied chains in isolation or in finite system volumes, but never with periodic boundary conditions. Finally, with the exception of early efforts to use the winding number for classifying knotting states,\(^\text{23}\) no studies have attempted to make a connection between knot statistics and the entanglement length, which is the goal of the present work.

2.1 Unknot probability

Previous studies of polymer knots have focused on the unknot probability \( p_0 \) for long polymer rings confined in a box (mostly on a lattice), and found \( p_0 \) to be proportional to \( e^{-N_{\text{N}}/N} \). On this basis, it has been argued that the probability of finding any particular knot in an increasingly long ring must also fall off as \( e^{-N_{\text{N}}/N} \).\(^\text{24}\) We will focus instead on values of \( p_0 \) for rings in periodic boxes.

Consider a box containing a single ring of length \( N \) in melt conditions, the box dimension therefore scaling with \( N^{1/3} \). We define the ring to be unknotted if it can be continuously deformed to a small loop without crossing itself or its periodic images. Configurations will almost always be unknotted for small \( N \), and almost always knotted for sufficiently large \( N \). Thus we expect a plot \( p_0 \) versus \( \log N \) to be somehow sigmoidal in shape, with values close to unity for \( N \) much smaller than \( N_{\text{c}} \) and approaching zero for \( N \) much larger than \( N_{\text{c}} \). The location of the transition region in the curve should be a good semi-quantitative indication of \( N_{\text{c}} \).

We might for example hope to phenomenologically define \( N_{\text{c}} \) such that
for some well-chosen constant $C$. To test this idea we would need to measure the unknot probability of rings in a volume with 3D periodic boundary conditions, which we are unable to do with our present methods. We can however carry out this program for chains in aperiodic, 1D, and 2D periodic boundary conditions. Thus, we can either estimate from these results the unknot probability curve for the 3D periodic case, or alternatively define a phenomenological criterion for $N_e$ directly from simulations on the other boundary conditions.

### 2.2 Topological entropy

The topological entropy $S_t$ measures the number of distinct topological states accessible to the system, defined as

$$S_t = -\sum_i p_i \log p_i,$$

where $p_i$ is the probability of finding the system in topological state $i$. If the system could access $N_e$ knots with equal probability, $S_t$ would equal $\log N_e$. For any nonuniform distribution, $S_t < \log N_e$ (Jensen’s inequality\(^{25}\)). Intuitively, we expect that the more entangled a system is, the more distinct topological states it can access when topologically equilibrated (i.e., when simulated so that chains can occasionally cross each other), hence the larger will be the topological entropy $S_t$.

The topological entropy depends on the total length of rings present; longer rings can tie more distinct knots. We expect $S_t$ to be proportional to $N/N_e$, which is large enough $N$. Crudely, we can think of the topological states of an entangled chain as the set of random walk configurations of its tube, with step size given by the entanglement length. The total number of such walks $\Omega$ can be approximated by representing the tube random walks on a lattice of obstacles, hence $\Omega \approx (z-1)^{N/N_e}$, with $z$ an effective coordination number ($z = 1$ excludes immediate backward steps). Hence $S_t = N/N_e \log (z-1)$ in this simple model. We shall make this calculation precise below.

We expect the linear dependence of $S_t$ on $N$ on quite general grounds; for sufficiently large $N$, the system can be divided into several sub-systems of equal size, each contributing an equal amount of entropy to the total, so that $S_t$ becomes an extensive quantity. (The contribution to the number of new states generated by joining subsystems is assumed to be small.)

The prefactor in this linear dependence can be made precise as follows. Consider a topologically equilibrated melt of entangled chains. The set of accessible configurations are ideal random walks; we measure entropy relative to this reference ensemble. This reference ensemble can be created in two steps: first generate an ensemble of topologically distinct tube arrangements, with tube diameter $a$ and average contour length $L$; second, fill the tubes with random walks. In this way, we recreate the equilibrium melt, so the entropy gain $S_t$ of creating topologically distinct tubes must cancel the entropy loss $S_t$ of confining random walk configurations inside the tube.

We compute $S_t$ by considering the chain within the tube to be a Gaussian coil pulled out to a contour length $L$ equal to $(N/N_e) a$, i.e., $N/N_e$ entanglement segments each of length $a$.\(^{26}\) Thus we have

$$p_0(N_e) = C \quad (1)$$

### 3 Simulation model

For our simulations, we use a coarse grained bead-spring model for polymer rings, following the approach of Grest and Kremer.\(^7\) The Hamiltonian\(^{29}\) includes a harmonic bond potential,

$$U_b = \frac{1}{2} k (r/\sigma - l_0)^2, \quad (4)$$

and a purely repulsive L-J pair potential for non-bonded pairs of beads.

$$S_t = -S_t = \frac{3}{2} \frac{L^2}{N a^2} = \frac{3}{2} \frac{N}{N_e} \quad (3)$$

We show in this work that eqn (1) and (3) can be used to estimate the entanglement length, and the results are reasonably consistent with otherwise heuristic methods. We simulated topologically equilibrated ring polymers at the melt density with Monte Carlo methods, to collect statistics on the distinct topological states visited by the system. We studied systems with different $N$ values under both aperiodic and periodic boundary conditions, to examine how the statistics varies with $N$ and to compare results with eqn (1) and (3). To carry out this program, we must overcome three challenges.

The first challenge is to simulate topologically equilibrated rings, which means that the system must be able to change topology with sufficient frequency. We achieve this by implementing various molecular restringing moves, which allow the rings to cross. Details of the simulation model and tests of the algorithm efficiency are presented in section 3.

The second challenge is to “teach” computers to identify distinct topological states. For this purpose, we use a powerful tool from knot theory, invariant polynomials. Here “invariant” means that the polynomial computed from a given ring configuration is the same for any deformation of the configuration that does not involve chains crossing each other. Among the invariant polynomials developed by knot theorists, we use the Jones polynomial,\(^{14,27}\) which is known to be a very good knot identifier and is also convenient to compute. The Jones polynomial can be constructed by a purely algebraic procedure from a ring conformation. Relevant details are given in section 4, where our emphasis is on the implementation of an efficient algorithm. Note that no invariant has yet been found that uniquely identifies all topologically distinct knots; in particular there exist distinct knots for which the Jones polynomial gives the same result. Hence, our topological entropy results are necessarily lower bounds.

The third challenge is to generalize the Jones polynomial to periodic knots, which we must do to study systems under periodic boundary conditions, in order to minimize the effects of free surfaces on the topological state. Intuitively, we expect that smaller systems will be required with periodic boundary conditions to reach the limit in which $S_t$ grows linearly with ring length. The Jones polynomial has been mostly discussed in the context of aperiodic knots, but was recently generalized by Grishanov,\(^{28}\) defined in terms of the bracket expansion (see section 4.3). We extend his approach to the use of skein relations (see section 4.2), which allows us to adapt the efficient Jones algorithms originally designed for aperiodic knots.
\[ U_p = 4\kappa [(r/\sigma)^{-12} - (r/\sigma)^{-6} + 0.25], \]

where \( \kappa = 400k_BT \), \( \epsilon = k_BT \), and \( \sigma = 1 \). The pair potential has a cutoff at \( r_c = 2^{1/6}\sigma \), the minimum position. It increases quickly from \( k_BT \) at \( r = \sigma \), to \( 10k_BT \) at \( r = 0.916\sigma \), so is a smooth but fairly rigid repulsive potential. We set the bead number density \( \rho \) to be 0.7\( \sigma^{-3} \), which results in a coordination number of about 9 excluding the bonded beads. These give us a model similar but not identical to the fully flexible model of Kremer and Grest.\(^9\)

This model and these values have been used to study binary homopolymer blends and diblock copolymer melts, and have been shown to represent the melt condition properly. The average bond length is about \( \sigma \), and the statistical segment length has been accurately determined to be 1.414, by measuring the \( N \) dependence of the radius of gyration, and by fitting it to the one-loop theory corrected scaling results.\(^{10}\)

We studied systems under both periodic and aperiodic boundary conditions. For the latter, we used a repulsive wall potential

\[ U_w = 4\pi \rho \sigma^3 \left[ \left( \frac{r}{\sigma} \right)^{-9} - 7.5 \left( \frac{r}{\sigma} \right)^{-3} + 2.5 \sqrt{10} \right] . \]

\( U_w \) is obtained by integrating \( U_p \) over a semi-infinite space outside walls, using the same density as that inside the box. \( U_w \) is cut off at its own minimum \( r = 0.85837\sigma \), and shifted such that it vanishes there. An internal truncation is used when energy exceeds about \( 80k_BT \), for both \( U_w \) and \( U_p \).

The cubic simulation boxes each contains a single ring with length \( N \) ranging from 100 to 1600. (In section 3.2 we briefly report on simulations of multiple-ring systems, to explore the efficiency of our simulation algorithm.) The box length is chosen such that the bead number density \( \rho \) equals 0.7\( \sigma^{-3} \). The box length along aperiodic dimension is increased on both sides by 0.7\( \sigma \), which is the size of the depletion region of the repulsion wall. The initial ring configuration is created by first making a random walk, then evenly distributing the end to end distance vector among all the bonds so that the ring closes.

We implemented several Monte Carlo moves to relax the local modes and sample the topological states of the system. Initially, a simple random bead displacement move is used to eliminate large overlaps of beads and therefore equilibrate the pressure. Then we use a combination of hybrid MC/MD move and various molecule rebridging moves. For the hybrid MC/MD move, first a short MD integration is performed, then the resulting configuration is accepted according to the Metropolis rule. The time interval is chosen such that the acceptance rate is greater than 0.9. Such moves do not change the entanglement topology (which we have verified explicitly) and are used for relaxing configurations locally. Finally we introduce rebridging moves to allow molecules to cross, and thereby change the topology. Rebridging moves are discussed in the next section.

All simulation work was carried out using the general purpose MC/MD simulation package Simpatico, developed by Morse and colleagues at University of Minnesota.\(^{31}\)

### 3.1 Rebridging moves

We implemented three types of rebridging moves to equilibrate the system topology: tetra-rebridge, octa-rebridge and double-tetra-rebridge. The first two are used for both aperiodic and periodic boundary conditions, while the last is designed only for periodic boundary conditions, in which different periodic images of a given molecule may cross.

To apply the tetra-rebridge move, a molecule is selected at random (we simulated boxes containing a single molecule, but this move works for many-ring system as well) and its aperiodic configuration is constructed. Then a list of groups of four beads (see Fig. 2(A)) are created such that: beads \( a \) and \( b \) are bonded, beads \( c \) and \( d \) are bonded, and the separations between all pairs \( a-b \), \( c-d \), \( a-c \), \( b-d \) fall into a prescribed range. The distance criterion is required to guarantee the detailed balance. One such group of four beads is then selected randomly, and the bonds \( a-b \) and \( c-d \) are removed and replaced with bonds \( a-c \) and \( b-d \). The new configuration is then accepted by comparing energies and applying the Metropolis rule.

Note that the beads must appear along the ring in the order \( a, b, c, d \). Otherwise, the rebridging of \( a \) to \( c \) and \( b \) to \( d \) will cut the original ring into two sub-rings. The construction of the aperiodic molecule shape is needed to avoid rebridging the molecule with one of its images, in which case the rebridging changes rings into periodic chains. The term “tetra” refers to the fact that four beads are involved and the four distances that are checked are on the edges of a tetrahedron.

The octa-rebridge move begins with a randomly chosen bead \( m \), which is bonded to beads denoted by \( a \) and \( b \), as shown in Fig. 2(B). The lengths of bonds \( a-m \) and \( b-m \) are checked to see if they both fall into the prescribed range. If yes, the neighborhood is further searched, to look for another such bonded triple bead group \( p-n-q \). Then six more distances \( p-n, n-q, p-m, q-m, a-n \) and \( n-b \) are checked. If they all fall into the same prescribed range, the rebridgings \( a-n-b \) and \( p-m-q \) are attempted, i.e., the

![Fig. 2](image-url)
bonding of beads $m$ and $n$ are exchanged, and the new configuration accepted according to the Metropolis rule. If multiple rebridging sites are found, only one is selected at random. This move is applicable to various situations: all beads on the same molecule, on different images of the same molecule, and on two different molecules. It has a relatively low acceptance rate compared to the tetra-rebridge move, since it needs to remove four old bonds and create four new bonds while the tetra-rebridge removes only two old bonds and creates only two new ones. The name “octa” refers to the fact that the eight bonds involved form an octahedron (see Fig. 2(B)).

The double-tetra-rebridge moves consists of two tetra rebridge moves applied to two closely approaching images of the same molecule; it is useful only when periodic boundaries are present. The move starts by constructing the aperiodic molecule configuration. Then the configuration is checked to see if any of its periodic images have two “close contacts” with it. In each close contact, two bonded beads on the image are close to two other bonded beads on the assigned configuration, i.e., they satisfy the same distance criteria as for a tetra-rebridge move (see Fig. 2(D)). The pattern of bond reconstruction is indicated in Fig. 2(D). Again, the move is accepted according to the Metropolis criterion.

We note the bead indices for a double-tetra-rebridge move must satisfy an ordering criterion: when walking along the backbone of the molecule, the bonded pair $a-b$ and $a'-b'$ must not be intercepted by either $c'-d'$ or $c-d$ pair (the ring configuration displayed in Fig. 2(D)) is the simplest case; more complicated configurations can be rebridged correctly by following this criterion. If that happens, the periodic ring will be cut into two periodic chains. Note that only two images are involved in this move. It is impossible to design a version that involve three images, such that two rebridging sites are between two different pairs of images.

In essence, tetra-rebridge move is the basis for the other two more complicated rebridging moves. The octa-rebridge move can be thought of as two sequential tetra-rebridge moves on two overlapped four-beads groups; we implemented it as a single move because it results in one portion of a molecule crossing another. Similarly, two sequential tetra-rebridge moves on two distant four-bead groups is equivalent to the double tetra-rebridge on the same image of the same molecule (see Fig. 2(C)). What we have implemented is the generalization to the case involving two images. The acceptance rates of these moves are generally low (0.4%, 0.02% and 0.02%, respectively, for the tetra, octa, and double tetra rebridge moves), however they are essential to permit the system to explore topologically distinct states, and are especially effective for the moderate systems we studied. Throughout this work, we choose the following Monte Carlo attempt rates: 40% tetra-rebridge, 30% octa-rebridge, 30% double-tetra-rebridge, and 0.2% hybrid MC/MD move.

### 3.2 Equilibrium tests

We use two quantities to verify the efficiency of molecular rebridging moves in equilibrating the system: the autocorrelation function of the slowest Rouse mode coefficients, and the variation with time of the radius of gyration.

The normalized Rouse modes for ring molecules can be shown to be,

$$R_s(t) = \left\langle A_p(t) A_p(0) \right\rangle / \left\langle A_p(0) A_p(0) \right\rangle$$

where $R_s(t)$ is the position of bead $n$ at time $t$. The $p = 0$ mode corresponds to the center of mass. The $p = 1$ modes represent the large scale conformation change: for two beads whose indices differ by $N/2$, sin $(2\pi pmN)$ and cos $(2\pi pmN)$ only change the sign, so $A_{p,s}$ and $A_{p,c}$ can be viewed as weighted averages of separation vectors for beads separated by a half of ring length, weights given by the magnitudes of sine or cosine functions. This is analogous to the spanning vector $R_s(t)$ defined by Kremer et al.,\textsuperscript{22} where $R_s(t)$ is given by $\left\langle (1/N) \sum_{n=1}^{N} (R_{in} - R_{i+N/2}(t)) \right\rangle$.

The autocorrelation functions of the Rouse mode coefficients are defined by:

$$R_s(t) = \left\langle A_p(t) A_p(0) \right\rangle / \left\langle A_p(0) A_p(0) \right\rangle$$

where $A_p$ is $A_{p,s}$ or $A_{p,c}$. The results of $R_s(t)$ for the two $p = 1$ modes, for systems under different boundary conditions, are shown in Fig. 3. For the aperiodic (0D), 1D and 2D periodic boundary conditions, we choose the ring length to be the largest system we studied. For the 3D periodic case, we choose a reference system containing 4 rings ($M = 4$) of length 800. Time is measured in units of $10^6$ Monte Carlo steps. For the 0D, 1D and 2D cases, $R_s(t)$ damps quickly to zero in a time less than $5 \times 10^6$. The damping of 3D reference system is slower, but still has a short correlation time, on the order of $6 \times 10^6$ Monte Carlo steps. The results on knots statistics discussed later are obtained from runs of length typically $10^7$ times this autocorrelation time.

To further demonstrate the ability of rebridging moves to equilibrate the system, we show in Fig. 4 the radius of gyration $R_g$ versus time for $N = 800$ and for $M = 4, 8, 16$ and 32 rings, all under 3D periodic boundary conditions (which is the most challenging to equilibrate topologically). The $R_g$ values are normalized by the isotropic random walk result $R_g = (N/12)^{1/2}$; one data point in this figure corresponds to $10^6$ Monte Carlo steps, the total length of $x$ axis in Fig. 3.

For $M = 4$ (yellow curve) and $M = 8$ (red curve) cases, $R_g/R_g$, values are fluctuating around 1, indicating that the rings are exploring isotropic random walks, not limited by topological constraints. The magnitude of fluctuations drops when $M$ is increased from 4 to 8, as expected. However, the system with $M = 16$ rings is only barely equilibrated during this simulation, and the $M = 32$ case is not equilibrated at all. All systems studied...
Section 3.2 describes the efficiency of our algorithms, organized as follows. Section 4.1 summarizes crossing diagrams and Reidemeister moves, which together form the basis for constructing knot invariants. Section 4.2 and Section 4.3 reprise two different approaches to computing the Jones polynomial, one based on the skein relation and another on the bracket summation.

Both approaches are documented in the literature; here we introduce a useful expression bridging the two approaches, which forms the basis of our algorithm for computing the Jones polynomial for periodic knots. Section 4.4 describes in detail how the Jones polynomial and the algorithms for its calculation are generalized to periodic systems. Readers only interested in our results obtained from the topological entropy may advance to section 5.

### 4 Identifying entanglement states

In this work, we use the Jones polynomial to identify distinct topological states. The Jones polynomial is known to be an excellent, but not complete knot identifier: two distinct knots occasionally share the same Jones polynomial. Thus the topological entropy we obtain using the Jones polynomial will be an underestimate of the true value. We use the Jones polynomial because it is at the same time a good knot identifier, and can be generalized to 1D and 2D periodic knots with relative ease.

This section presents details of computing the Jones polynomial for ring configurations, including the generalization to periodic boundary conditions, with an emphasis on relatively efficient algorithms, organized as follows. Section 4.1 summarizes crossing diagrams and Reidemeister moves, which together form the basis for constructing knot invariants. Section 4.2 and Section 4.3 reprise two different approaches to computing the Jones polynomial, one based on the skein relation and another on the bracket summation.

Both approaches are documented in the literature; here we introduce a useful expression bridging the two approaches, which forms the basis of our algorithm for computing the Jones polynomial for periodic knots. Section 4.4 describes in detail how the Jones polynomial and the algorithms for its calculation are generalized to periodic systems. Readers only interested in our results obtained from the topological entropy may advance to section 5.

#### 4.1 Crossing diagram and reidemeister moves

Knots can be represented in terms of crossing diagrams. A crossing diagram for a polymer can be thought of as resulting from compressing the polymer against an impenetrable surface, without allowing the chain to cross itself. A closed curve in a crossing diagram then corresponds to a closed loop in the knot, and is called a component. Walking along a component, we encounter a succession of crossings. The curves may be thought of as a sequence of segments, each of which participates in one crossing. Self crossings are those for which the two crossing segments belong to the same component.

The crossing diagrams for the examples in Fig. 1 are shown in Fig. 5 (arrows are used to orient components, which is needed to construct the Jones polynomial, as explained in section 4.2). These examples all involve a single ring. Analogous to spreading a loosely tangled string at a tabletop, a crossing diagram for a single ring is then a continuous closed curve in the plane, that may cross over or under itself multiple times. A break in the curve at a crossing indicates an undercrossing segment.

Crossing diagrams can be generalized to 1D and 2D periodic systems straightforwardly. But for the 3D periodic system, it is not apparent how to pick up the projection direction. So throughout this work, the identification of topological states are restricted to aperiodic, 1D and 2D boundary conditions.

Reidemeister moves are operations on crossing diagrams that do not change the topology, i.e., that correspond to moving the segments without allowing the path to cross itself. Type 1 (Fig. 6(a)) move creates or annihilates a simple twist. Type 2 (Fig. 6(b)) move involves two sections, and creates or annihilates two superficial crossings between them. Type 3 (Fig. 6(c)) move involves moving one section from one side of a crossing to the opposite side.

The crossing diagrams of two apparently different but topologically identical knots can always be brought into each other by a sequence of Reidemeister moves (Reidemeister theorem).

#### Fig. 5 The oriented crossing diagrams for the knots shown in Fig. 1.
Thus knot invariants such as the Jones polynomial are invariant with respect to the Reidemeister moves. A simple example of a knot invariant is the minimum crossing number, which is a crude indicator of knot complexity, and is used to index knots in standard tables.

Type 1 and type 2 moves can be applied in a “downhill” direction towards a simpler crossing diagram, always decreasing the number of crossings. We shall use this property to design an algorithm for simplifying the crossing diagram. In contrast, there is no obvious “downhill” direction to apply the type 3 move.

4.2 Skein relation

The Jones polynomial is defined for an oriented crossing diagram, which is obtained by walking along the components of a crossing diagram and adding arrows to the segments. With segments oriented, we can introduce the crossing signs. A crossing has a positive sign if, by a counterclockwise rotation, the upper segment at the crossing first overlays the lower segment with the same orientation (see the crossing in Fig. 7, \( K_+ \)), and a negative sign if otherwise (see the crossing in Fig. 7, \( K_- \)). The summation of signs of crossings is called writhe and denoted by \( W \). The mirror image of a crossing diagram is obtained by changing the signs of all crossings (exchanging \( K_+ \) and \( K_- \)).

Each component in a crossing diagram can be oriented in two ways. This freedom of orientation does not matter for single component crossing diagrams since the crossing signs do not change, but may matter for multi-component cases. In our simulations, the crossing diagrams are oriented in the direction of increasing bead indices.

One way to define the Jones polynomial is in terms of the skein relation. The skein relation involves the Jones polynomials of three crossing diagrams that differ at just one crossing, as highlighted in Fig. 7 (the shaded areas represent identical but unspecified portions of the three crossing diagrams). For diagrams \( K_+ \) and \( K_- \), the crossing signs are positive and negative, respectively. For diagram \( K_0 \) the crossing is eliminated while the arrow directions are preserved. Denote the corresponding Jones polynomials by \( V_{K_+} \), \( V_{K_-} \), and \( V_{K_0} \). The skein relation reads

\[
a^4 V_{K_0}(a) - a^{-4} V_{K_+}(a) = (a^{-2} - a^2) V_{K_-}(a). \tag{10}
\]

(Note that we used the conventional \( a \) as the argument to the Jones polynomial,\(^{33} \) which should not be confused with the tube diameter.)

The skein relation can be used to construct a relatively efficient recursive algorithm for computing the Jones polynomial of a knot from its crossing diagram. The algorithm we summarize below for completeness was developed by Ochiai. His group has developed a package\(^{44} \) for studying knots; we reverse-engineered their algorithm from the publically available source codes.

Applying the skein relation to any crossing in a crossing diagram \( (K_+ \text{ or } K_-) \), we can always express the corresponding Jones polynomial as a summation of Jones polynomials of two related diagrams, one differing from the original by a single crossing sign \( (K_0 \text{ or } K_0) \) and another with one less crossing \( (K_0) \), with multiplicative factors given by the skein relation.

To use this skein relation to efficiently compute the Jones polynomial, we first locate the shortest subloop in the crossing diagram, i.e., the subloop with least number of crossings. If all its crossings are of the same sign, the subloop can be shown to be unentangled, and can be removed by Reidemeister moves, thus simplifying the crossing diagram. If its crossings are of mixed signs, we can disentangle the subloop by “pushing” it up above or down below all other segments, using eqn (10). To decide whether pushing crossings up or down is more efficient, we count the numbers of positive and negative crossings separately; whichever set is smaller are the “active” crossings to be eliminated. In what follows we assume the active crossings are positive.

We then choose one active crossing and apply the skein relation on it, which generates two new crossing diagrams whose Jones polynomials are related to the original. The original crossing diagram is of type \( K_+ \) as in Fig. 7, and the two new diagrams are of types \( K_- \) and \( K_0 \) respectively. \( K_0 \) is simpler than \( K_+ \), since one crossing has been eliminated. \( K_+ \) has the same number of crossings as \( K_- \), but is simpler in that the subloop we are working on has fewer crossings to be “pushed”.

To continue, we choose another positive crossing on the same subloop of \( K_+ \) and proceed as before, which generates two new diagrams of types \( K_- \) and \( K_0 \). We continue in this fashion until the active subloop has only negative crossings, at which point it can be eliminated using Reidemeister moves. Along the way, we generate various smaller crossing diagrams (type \( K_0 \) at each step) to which the same algorithm can be recursively applied. In the end, we obtain a set of crossing-free diagrams, whose Jones polynomials, multiplied by the factors accumulated from successive applications of the skein relation, can be summed to give the original Jones polynomial.

The Jones polynomials of these crossing-free diagrams are specified by the following rules. A single free loop or unknot is assigned a Jones polynomial of unity; for each additional free loop, a loop factor

\[
d = -(a^2 + a^{-2}) \tag{11}
\]
is assigned. These rules complete the definition of the Jones polynomial.

The skein relation is compatible with the Reidemeister 2 and 3 moves, as can be seen by applying it to the involved diagrams directly. With the loop factor given by eqn (11), it can also be shown that the skein relation is consistent with the Reidemeister 1 move, by applying it to a simple twist. This compatibility demonstrates that the Jones polynomial is a topological invariant.

The above-described Ochiai approach is relatively efficient because of the partially “directed” nature of the simplifications; we are constantly identifying those subloops that are easiest to disentangle, and removing them from the crossing diagram by skein moves. As a side effect of these moves, however, new but simpler \( K_0 \) type diagrams are generated, which must also be processed in the same way. The worst-case performance of this algorithm appears to be exponential in the number of crossings, though there is a large variation in the execution time for different crossings, to obtain \( 2^n \) new crossing diagrams, each containing a set of free loops (with no crossings). If we assign the value \( f = 1 \) to an unknot, and a factor \( d = -(a^2 + a^{-2}) \) to each additional free loop as before, we can sum the contributions from these \( 2^n \) states (with proper multiplicative factors derived from eqn (13)) to obtain \( f_K \) for the untwisted knot of Fig. 1 to be \( a^3 + a^{-8} - a^7 - a^{-4} + 1 \).

### 4.3 Jones polynomial: bracket expansion

An alternate definition of the Jones polynomial can be given in terms of the bracket expansion. It turns out that we need to use both the skein relation and the bracket expansion to efficiently compute the generalized Jones polynomial for knots in periodic boundary conditions. Thus, we briefly reprise the bracket expansion here.

Defining the Jones polynomial using the bracket expansion makes use of a related polynomial \( f_K \) defined for non-oriented crossing diagrams. Consider three non-oriented crossing diagrams that differ at only one crossing, as shown in Fig. 9. \( f_K \) is defined by the bracket expansion, which is a recursive relation of the form

\[
 f_K(a) = af_K(a) + a^{-1}f_K(a).
\] (13)

The two diagrams on the right are simpler than the original one, since they each contain one less crossing. Thus for a crossing diagram with \( n \) crossings, we can apply the bracket expansion to all the crossings, to obtain \( 2^n \) new crossing diagrams, each containing a set of free loops (with no crossings). If we assign the value \( f = 1 \) to an unknot, and a factor \( d = -(a^2 + a^{-2}) \) to each additional free loop as before, we can sum the contributions from these \( 2^n \) states (with proper multiplicative factors derived from eqn (13)) to obtain \( f_K \) for the original diagram. \( f_K \) so defined is invariant with respect to Reidemeister 2 and 3 moves, as can be shown by explicitly evaluating \( f \) for crossing diagrams on both sides of the moves depicted in Fig. 6.

The relation between \( f_K \) so defined and the Jones polynomial \( V_K \) is determined by enforcing Reidemeister 1 invariance of \( V_K \). To check the effect of the Reidemeister 1 move, we apply the recursion relation eqn (13) to the crossing at a simple twist and use the loop factor \( d \). The result shows that \( f(a) \) for the untwisted state is equal to the twisted one multiplied by a factor \( -(a^2 + a^{-2})^s \), where \( s \) is the crossing sign. Thus \( -(a^2 + a^{-2})^s f(a) \) is invariant with respect to the Reidemeister 1 move. Generalizing this to all crossings (not just those at twists), and noticing that the summation of signs of all crossings gives the writhe, motivates the definition:

\[
 V_K(a) = (a^2 - a^{-2})^{-\text{writhe}} f_K(a).
\] (14)

\( V_K \) so defined is invariant with respect to all Reidemeister moves.

Furthermore, it can be shown directly that \( V_K \) satisfies the skein relation (eqn (10)) introduced in the section 4.2.
(see Appendix A), and so is indeed the same as the Jones polynomial defined earlier. Thus eqn (14) provides an alternative way to compute the Jones polynomial.

Eqn (14) also makes clear the relation between the Jones polynomial of a knot $K$ and its image $K^\prime$, namely $V_K(a) = V_{K^\prime}(a^{-1})$. (We have $f_K(a) = f_{K^\prime}(a^{-1})$ as a consequence of the bracket expansion, and $w_K = -w_{K^\prime}$.)

To work with Jones polynomial directly, we invert eqn (14) and rewrite eqn (13) as

$$V_K(a) = (a^{-1})^{w_K} V_K(a) + (a^{-1})(a^{-1})^{w_K} V_{K^\prime}(a).$$

This equation involves the Jones polynomial of three oriented diagrams. To compute the Jones polynomial $V_K(a)$ of an oriented diagram $K$ with writhe $w_K$, we proceed as follows. We erase orientations in $K$, select a crossing, and create two new bracket states $K_+$ and $K_-$ by replacing this crossing with two new crossings (see Fig. 9). We then add orientations to the resulting crossing diagrams, which have Jones polynomials $V_{K_+}$ and $V_{K_-}$, and writhes $w_{K_+}$ and $w_{K_-}$. (The writhes and Jones polynomials of $K_+$ and $K_-$ depend on how the diagrams are oriented, but the final result for $V_K$ does not depend on the orientation. See Appendix A.)

When evaluating the Jones polynomial for aperiodic knots, we can freely switch the use of skein relation and bracket expansion. However, as we have commented, when implemented by brute force, the time to compute the Jones polynomial by bracket expansion scales with $2^n$, where $n$ is the number of crossings. This quickly becomes impractical. Whereas, the Ochiai algorithm based on the skein relation is “directed”, as explained in section 4.2; which permits us to evaluate the Jones polynomials for crossing diagrams involving several hundreds of crossings.

For aperiodic knots, the skein relation is both sufficient and efficient, and thus preferred. For periodic knots, as we shall show in the next section, the skein relation does not suffice to reduce all crossing diagrams to simple end states. As a result, we must occasionally use the bracket expansion for periodic knots, switching back to the skein relation whenever possible.

### 4.4 Periodic knots

In this section, we describe how the ideas and methods of computing the Jones polynomials for aperiodic knots are generalized to 2D periodic knots. Our approach makes use of recent work of Grishanov, who first extended the bracket expansion to compute the Jones polynomials for periodic textile patterns (a subset of periodic knots in which all strands form continuous lines).

Ring configurations in 2D periodic boundary conditions can be viewed as periodic knotted patterns which yield periodic crossing diagrams when projected along the $z$ direction. A simple example, a “chain mail” pattern, is shown in Fig. 10. This periodic pattern can be represented by a unit cell; every crossing in the periodic diagram appears only once in the unit cell. The choice of unit cell is not unique: two possible choices are shown in Fig. 10 (the dashed square and parallelogram). Examples of unit cells of a few simple periodic knots containing a single loop are shown in Fig. 11.

#### 4.4.1 Torus diagram

For periodic crossing diagrams, we interpret the various transformations associated with Reidemeister moves, the skein relation, and bracket summation, as operating simultaneously on all periodic copies of the unit cell. In this regard, it is convenient to introduce a torus diagram, which is constructed by wrapping the unit cell along both $x$ and $y$ directions, and joining the matched crossings of the unit cell boundaries (see Fig. 12(a) and 12(b)). For the 1D periodic case, we have a cylinder diagram. A single operation on the torus diagram corresponds to simultaneous operations on all periodic images of the unit cell.

There exist examples of periodic crossing diagrams which cannot be simplified by using the skein relation alone. For instance, consider the diagram labeled as $B$ in Fig. 13 (2 in Fig. 11). Applying the skein relation to the bracelet $B$ generates two states $B_1$ and $B_2$. The $B_2$ state can be thought of as a free loop in torus diagram, or a set of disentangled free loops when viewed in the periodic scheme. The $B_1$ state contains two non-intersecting curves after an untwist move. These curves can be thought of as loops wrapping azimuthally around the torus, or as non-crossing lines in the periodic zone. The question is: what polynomial weight should be assigned to these components?
Fig. 12 Unit cell and corresponding torus diagram for chain-mail pattern of writhe 0.

If we give these lines the same loop factor as the free loops, eqn (11), we do not obtain a good knot identifier, since effectively this is the same as passing a wrapping loop through the torus so that it sits on the surface of the torus. If such an operation were allowed, we could perform it before using the skein relation, and the bracelet then becomes an unknot after two untwisting operations. In a similar way, examples (b), (c), in Fig. 11 would reduce to a trefoil, and examples (d), (e), (f) to an unknot. (A wrapping line may be viewed as equivalent to an aperiodic torus knot.\textsuperscript{44})

Grishanov\textsuperscript{44} proposes that the periodic lines wrapping around the torus should be treated as topologically distinct objects. Different wrapping loops are distinguished by the numbers of turns they make around the body or the center of the torus (equivalently, the numbers of times they cross the periodic boundaries). These pairs of numbers are called wrapping indices, and may be thought of as 2D integer vectors. Knots in general do not have a single set of wrapping indices.

To count the wrapping indices, we orient each component in an arbitrary way, and assign integers 1, –1, 1 and –1 to the segments at boundary crossings +x (crossing the right edge of unit cell), –x (crossing the left edge), +y (crossing the upper edge) and –y (crossing the lower edge), respectively. The summation of the values for +x and –x crossings gives the first wrapping index, and that for +y and –y gives the second. These two numbers are coprime (i.e., have no nontrivial common factors), since the unit cell represents the smallest repeating unit. They are defined up to an overall sign, depending on how a component is oriented. Following Grishanov, we always take the y indices to be positive, and the x indices positive if the y indices vanishes. Closed components always have wrapping indices equal to (0, 0).

Using the bracket expansion, we can express the Jones polynomial of a given diagram as a summation of Jones polynomials of a set of crossing-free “final states”, whose components are either free loops or wrapping lines. The free loops each contribute the usual loop factor to the Jones polynomial. The wrapping lines are represented by wrapping indices, described above. The indices of all wrapping lines in a single final state must be identical, else they would cross.

Thus the Jones polynomial of each final state may be written as

\[ d^{–\delta_{0,0}} (\alpha \theta, \beta) \]  \tag{16}

where \( d \) is the free loop factor, \( \gamma \) the number of free loops, \( \theta \) the number of periodic lines, and \( (\alpha, \beta) \) the wrapping indices. The factor \( \delta_{\alpha,0} \delta_{\beta,0} \) is chosen such that the Jones polynomial of an unknot equals unity (here we differ from Grishanov’s convention). Summing contributions from all final states, we obtain the extended Jones polynomial for a 2D periodic knot as

\[ V(a) = \sum_i P_i(a) d^{–\delta_{\alpha_i,0}\delta_{\beta_i,0}} (\alpha_i \theta_i, \beta_i \theta_i) \]  \tag{17}

where \( i \) runs through all final states, and \( P_i \) are accumulated multiplicative factors derived from skein or bracket summation steps. (Terms with the same wrapping indices are summed, leading to the factor \( \theta_i \).) Applied to aperiodic knots, this expression reduces to the usual Jones polynomial.

To generalize the Ochiai algorithm to periodic knots, three modifications are needed. First, subloops are allowed to have boundary crossings. This means, when visualized in the periodic zone, subloops may traverse several unit cells, as long as the +x and –x, and +y and –y boundary crossings cancel.

Second, not every subloop involving boundary crossings can be disentangled by just using the skein relation, e.g., the examples shown in Fig. 14. Applying skein relation to \( X_+ \) and \( X_- \) changes them forward and backward indefinitely. In such a case, we must employ the bracket expansion, which in the present example generates two wrapping loops and one free loop on the torus diagram. We thus incorporate the bracket expansion into our algorithm, and invoke it only when the skein relation fails to further simplify the crossing diagram.

Third, note that a subloop involving boundary crossings can be freed if its infinite periodic copies in the periodic scheme meets the following “stacking rule”: the copies on the right are consistently above or below the ones on the left, and the copies on the top are consistently above or below the ones at the bottom. This arrangement is analogous to layering a deck of cards in an overlapping column, followed by layering multiple copies of the column into overlapping rows. Recall that when our algorithm is applied to the aperiodic knots, the shortest subloops are freed by arranging the crossings to have the same sign by applying the skein relation. Analogously for the periodic cases, the skein relation is applied to achieve the arrangement satisfying the stacking rule.

Example 2. To illustrate the procedure of computing Jones polynomial for a periodic knot, consider the knot \( 5_1 \) (w = 5) in

\[ X_+ \quad X_- \]

Fig. 14 A simple crossing for which the Jones polynomial cannot be evaluated using the skein relation alone.
4.4.2 Twist invariance. Starting from the same periodic knotting pattern, the wrapping indices of final states depend on the choice of unit cells, even though the polynomial prefactor does not. This can be seen by viewing the crossing diagram in the “extended zone” scheme (obtained by duplicating the unit cell along both x and y directions). Suppose after a series of simplifications to the original periodic pattern, we obtain a final state containing one single wrapping component, as shown in Fig. 16. Now consider the effect of two possible choices of unit cell. The wrapping indices are (1, 1) when the unit cell labeled $a$ is used, and (0, 1) when the one labeled $b$ is used. But both choices represent the same knotting pattern.

In the simulations, the 2D projection of simulation box provides a natural choice of unit cell. But we encounter a similar problem: if we rotate a knotting pattern by some commensurate angle, the wrapping indices are changed. Such changes are associated with the rotational degree of freedom, and should not contribute to the topological entropy. We need a way to identify Jones polynomials arising from different choices of unit cell as topologically identical.

The solution was suggested by Grishanov, who introduced a canonical choice of unit cell for a set of wrapping indices. To define this canonical form, consider how the wrapping indices vary with choices of unit cell. It turns out (see Appendix B) that changing the unit cell corresponds to multiplying the 2D vectors of wrapping indices by a $2 \times 2$ matrix $U$ with integer entries and unit determinant (to preserve the area of the unit cell). In other words, $U$ belongs to the set $SL_2(\mathbb{Z})$ (also called the modular group). Thus for each given set of vectors $\{v_i = (\alpha_i, \beta_i)\}$, there exist infinite number of partner sets, each related to the original by multiplying by a $U$ matrix, or equivalently a change in the choice of unit cell.

Following Grishanov, we choose the canonical set to be the set $\{U \cdot v_i\}$, such that $U$ minimizes the quadratic form:

$$Q(U, \{v_i\}) = \sum_i (U \cdot v_i) \cdot (U \cdot v_i)$$

Our minimization algorithm is sketched in Appendix B.

4.5 Implementation

We have described above how we have extended the Ochiai algorithm to compute the Jones polynomial for knots in periodic boundary conditions, by performing one bracket expansion step whenever further progress in simplifying a crossing diagram cannot be made using only the skein relation. In addition, for 2D periodic boundary conditions, we must transform the wrapping indices into canonical forms. (Wrapping indices of 1D periodic knots are uniquely defined, so there is no need to make “canonical”.)

Simulated polymer configurations typically contain a large number of spurious crossings, which slows down our algorithm significantly. Before generating a crossing diagram, we simplify the polymer configuration by using a method adapted from the Z algorithm for primitive path analysis. The method, which we call triangular reduction, straightens two consecutive bonds in the configuration if the triangle spanned by the bonds does not intercept any other bond. This turns out to be very helpful for the large systems. Even with this technique, our algorithm for computing the Jones polynomial becomes impractically slow for rings of more than 1000 or so beads. Fortunately, rings of this length are sufficiently entangled to be representative of long chains, as we shall see in the next section.

All periodic knots with up to four crossings, and one example with five crossings, are shown in Fig. 11. Their Jones polynomials and writhes are listed in Table 1. Only positive writhe values are
shown, since knots with negative writhes correspond to the mirror images of knots in the table. Note that the chain-mail pattern has two possible knots (41 and 42), depending on the sign of crossings.

Grishanov focused on periodic patterns relevant to the textile industry, in which patterns the components are all continuous threads. In our work, we always start from closed components, so our “simple” examples are different from his. Looking at Table 1 more carefully, we notice that the wrapping indices are always even, which again results in exponents that are even. The odd power of \( C_0 \) is balanced by the change in the number of components: if two line components are present, the wrapping indices are still multiples of 4. When line components are present, crossings with \(+\) type boundaries often result in exponents that are even. The wrapping indices are always even, the number of loop factors are always odd multiples of 2 (as confirmed by reading Table 1). To see this, consider the effect on the polynomial factors of applying the skein relation or bracket expansion can change the number of boundary crossings. Reidemeister moves that cross the boundary always remove boundary crossing in pairs (\(+x\) and \(+x\), \(+y\) and \(+y\) boundaries). Neither the skein relation or bracket expansion can change the number of boundary crossings. Reidemeister moves that cross the boundary always remove boundary crossing in pairs (\(+x\) and \(+x\), \(+y\) and \(+y\) boundaries). Neither the skein relation or bracket expansion can change the number of boundary crossings. Reidemeister moves that cross the boundary always remove boundary crossing in pairs (\(+x\) and \(+x\), \(+y\) and \(+y\) boundaries). Neither the skein relation or bracket expansion can change the number of boundary crossings.

Moreover, it can be shown that the exponents of monomials in the polynomial for components with indices \((0, 0)\) are always multiples of 4, while those associated with line components are always odd multiples of 2 (as confirmed by reading Table 1). To see this, consider the effect on the polynomial factors of applying the skein relation. We start from 1 (\(= a^0\)) for any crossing diagram. Flipping the sign of some crossing multiplies the polynomial by \(a^0\) or \(a^{-8}\), so the exponents remain multiples of 4. Reconnecting the arrow to obtain the \(K_0\) state (see Fig. 7) multiplies the polynomial by terms of odd powers of \(a^2\). This is balanced by the change in the number of components: if two segments at the crossing are on the same component, the reconnecting operation creates a new component; whereas, if two segments are on different components, the reconnecting operation annihilates one of them.

So the number of components is changed by +1 or –1, which changes the exponent of the loop factor (\(a = -(a^2 + a^{-2})\)) by +1 or –1, and effectively changes the exponents of all monomials by an odd power of \(a^2\). Thus the exponents after applying the skein relation are still multiples of 4. When line components are present, we lose the compensation from loop factors, but since the number of line components are always even, the number of loop factors are also even, which again results in exponents that are even. The difference between \((0, 0)\) components and line components is caused by our choice of convention in eqn (17) (chosen so polynomials for aperiodic knots reduce to the usual conventions). A similar analysis applies to bracket expansion as well.

### 5 Results

We have performed extensive Monte Carlo samplings of topological states for systems containing a single ring polymer confined under aperiodic, 1D and 2D periodic boundary conditions, and collected the distribution of topological states as defined by the Jones polynomial. For each ring length and type of boundary condition, we sampled more than \(10^7\) configurations and obtained up to several million distinct topological states or knots, after an effort of a few months of parallelized simulations on 16 processors. The results are presented below: first the unknot probability, then the states distribution and the topological entropy.

#### 5.1 Unknot probability

Unknot probability has been extensively studied in the literature, but only for systems under aperiodic confinement. Here we report results obtained under periodic boundary conditions as well, shown in Fig. 17, which include three data sets, corresponding to aperiodic, 1D and 2D periodic boundary conditions. The curves connecting data points all follow a similar trend: equal to unity for \(N < 10\), decreasing monotonically inside a well-defined transition zone, and dropping to zero as \(N\) becomes large.

This trend is in accord with previous studies on aperiodic knots, for short rings, majority configurations are unknotted, while for longer rings, typical configurations are almost always knotted. We extend these previous results with our unbiased Monte Carlo sampling of topologically equilibrated rings under melt conditions, for both aperiodic and periodic boundary conditions.

#### Fig. 17 Ring length dependence of unknot probabilities, for aperiodic (apbc), 1D and 2D periodic boundary condition.
Boundary effects are evident in Fig. 17. The location of the transition zone is shifted to smaller \( N \) as we reduce the surface effect by moving from aperiodic to 1D and 2D periodic boundary conditions. Each time we make an additional dimension periodic, the rings have more opportunity to become entangled with their images across the periodic boundary.

We do not have results for 3D periodic case, but the corresponding curve should be shifted further to the left. The dashed line in the figure is a guess as to the 3D result. (Since the difference between the aperiodic and 1D results are greater than that between the 2D and 1D results, the difference between the 3D and 2D results is likely less than or comparable to the latter.)

If we use the dashed curve as a reasonable guess to the 3D behavior, and use eqn (1) with \( C = 1/2 \) to estimate the entanglement length, we obtain a value of \( N_e = 90 \).

To compare this value to that estimated using the chain shrinkage algorithm of ref. 19, we map the entanglement length of their model onto ours. Our bead spring model is very similar to their fully flexible model, which has a density \( \rho = 0.85\sigma^{-3} \), and a packing length \( p = \frac{1}{10}\rho\sigma \). The entanglement length they found is \( N_e, \sigma = 70 \pm 10 \) from the plateau modulus, and is \( N_e, pp = 65 \pm 7 \) using primitive path analysis. (Finite length effects lead to a slightly higher \( N_e \) value than reported in ref. 19.)

The Lin-Noolandi ansatz states that the number of entanglement strands in a single entanglement volume is a constant \( B \):

\[
B^{1/2} = \frac{\rho a^3}{N_e} = N_e^{1/2} b^3 = N_e^{1/2}
\]

The ansatz implies that \( N_e \rho^2 b^6 = N_e (\rho p)^3 \) is a universal constant.\(^{19}\) Based on this, and using our values of the density and the statistical segment length \( \rho = 0.7 \sigma^{-3} \) and \( b = 1.414 \sigma \), we found \( N_e \) in our system is 0.955 times that of the fully flexible model of ref. 9. Using \( N_e, \sigma \) or \( N_e, pp \) for their value, we obtain corresponding values of \( N_e = 67 \pm 10 \) or \( N_e = 62 \pm 7 \) for our system. Compared to this, the value \( N_e = 90 \) we obtained using the unknot probability is a bit large, but reasonably close.

Alternatively, we can say that \( P(d, a, N) = 1/2 \) for some once-adjustable constant \( a \), and use the 2D periodic results for the unknot probability to infer \( N_e \) rather than trying to guess the 3D unknot probability. We have \( P_4(150) \) very nearly equal to 0.5 for the 2D results; hence a value of \( \alpha = 150/65 \) or about 2.3 is suggested. This value of \( \alpha \) could then be used to estimate \( N_e \) for systems with chains of different stiffness or bulkiness.

5.2 Knotting probability distribution

Before presenting results on the entropy, it is instructive to look at how the probability of a particular knot varies with ring length. We examine as examples a few simple prime knots (3-1, 4-1, 5-1, 5-2, and 6-1), and one composite knot (3-1#3-1, formed by tying two 3-1 knots in sequence on a single ring). Fig. 18 displays the occurrence probabilities of these knots as a function of ring length for aperiodic boundary conditions. (These curves were obtained from examining more than 10\(^7 \) configurations.)

Unlike the unknot probability, which decreases monotonically, these curves all have a maximum, which moves progressively outwards for knots of increasing complexity (measured in terms of the minimum number of crossings). This may be understood as follows: when \( N \) is too small, a ring must stretch and thus lose configurational entropy to tie a given knot, so the probability is low to find the knot; whereas when \( N \) is too large, many knots are easily tied, so the probability of any given knot will decrease. These results are consistent with previous studies.\(^{40}\)

Fig. 19 shows the probability to observe the first few knots, with different curves corresponding to rings of different length. The abscissa are arbitrary integer labels assigned to recognized knot types, ordered by minimum crossing number. These probabilities decrease quickly with crossing number; we show the results over a wider range in the inset. For knots that are chiral (see caption of Fig. 1), e.g., 3-1, we also show the probabilities for their mirror images, which are nearly identical, as expected.

We see clearly that as \( N \) increases, the distributions spread out. Sampling these distributions well becomes increasingly difficult as \( N \) increases. The difficulty in sampling is especially evident in Fig. 20, where rank-ordered state probabilities are plotted semilog. The probability distribution for accessible knots is far from uniform; there is an approximately exponential tail of increasingly rare states. For rings longer than \( N = 200 \), there are many states with probability \( p \) less than \( 10^{-6} \) (i.e., \( \ln p < -13.8 \)).
Fig. 20  Rank ordered state probability for the aperiodic boundary conditions.

Though each of these rare states contribute a small fraction of entropy, collectively they are non-negligible.

5.3 Error analysis for $S_i$

In principle, computing the topological entropy $S$ from the probability distribution for knots is simple; just apply eqn (2). But the preceeding discussion of Fig. 20 makes clear that the key to computing $S$ is to sample the probability distribution well enough, and furthermore to estimate the errors that arise from incomplete sampling.

There are three sources of error in computing $S$ in this way: 1) in a finite sample of different knots, there will be fluctuations in the number of times each knot appears; 2) in a finite sample, there may likewise be accessible knots that are missed completely; and 3) the Jones polynomial will sometimes give the same result for topologically distinct knots. Below, we will analyze the first two sources of (statistical) error, and make what arguments we can about the third source of (systematic) error.

Our essential results are presented in Tables 2, 3, and 4, for the three types of boundary condition. The tables report the ring length $N$, number of samples, the number of distinct knots found, and entropy $S$ computed directly from eqn (2) in the first four columns. For the largest systems studied, we accumulated more than $4 \times 10^6$ topological states. For the aperiodic case (Table 2), the third and fourth columns also report ratios of values given by using the Jones and HOMFLY polynomials respectively as knot identifiers.

The HOMFLY polynomial $P_K(t, z)$ is another invariant defined for aperiodic knots. Briefly, $P_K(t, z)$ can be defined by a skein relation analogous to eqn (10): $t^{-i} P_K(t, z) - i P_K(t, z) = z P_K(t, z)$, and calculated using a similar algorithm as for the Jones polynomial. The closing condition is such that $P(r, z) = 1$ for an unknot and a loop factor $d = (t^{-i} - t)z^{-1}$ is assigned for each additional free loop. The HOMFLY reduces to the Jones polynomial (in our convention) if we set $t = a^{-1}$ and $z = a^{-2} - a^2$.

Like the Jones polynomial, the HOMFLY polynomial is an imperfect (but somewhat better) knot identifier. We did not use HOMFLY in this work, because it has not been generalized to periodic knots. The results of Table 2 suggest that compared to the HOMFLY polynomial, the Jones polynomial misidentified knots about 15% of the time, which leads to errors in entropy of at most 3%, for the ring lengths studied. Of course, we do not know how often the HOMFLY polynomial itself mistakes one knot for another; but it provides some comfort that upgrading our knot identifier from Jones to HOMFLY does not change the entropy very much.

We now return to consider the statistical errors in computing $S_i$ from eqn (2). The first source of error, fluctuations in the number of times each knot appears in a large but finite sample, can be analyzed by assuming Poisson statistics for sampling among many possible knots. If we assume we know exactly the

<table>
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<th>$N$</th>
<th># Samples</th>
<th># States (%)HOMFLY</th>
<th>$S$ (%HOMFLY)</th>
<th>$\sigma(S)$</th>
<th>$S_c$</th>
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<td>12, 032</td>
<td>19 (100%)</td>
<td>0.092 (100%)</td>
<td>2E-4</td>
<td>0.092</td>
</tr>
<tr>
<td>200</td>
<td>12,800,032</td>
<td>175 (99%)</td>
<td>0.466 (100%)</td>
<td>3E-4</td>
<td>0.466</td>
</tr>
<tr>
<td>400</td>
<td>12,220,032</td>
<td>4,670 (86%)</td>
<td>1.492 (100%)</td>
<td>5E-4</td>
<td>1.492</td>
</tr>
<tr>
<td>600</td>
<td>12,797,340</td>
<td>47,974 (81%)</td>
<td>2.807 (99%)</td>
<td>9E-3</td>
<td>2.834</td>
</tr>
<tr>
<td>800</td>
<td>12,598,850</td>
<td>217,116 (80%)</td>
<td>4.382 (98%)</td>
<td>1E-3</td>
<td>4.486</td>
</tr>
<tr>
<td>1000</td>
<td>5,111,599</td>
<td>382,489 (84%)</td>
<td>6.350 (98%)</td>
<td>3E-3</td>
<td>6.641</td>
</tr>
<tr>
<td>1200</td>
<td>11,976,190</td>
<td>1,743,954 (85%)</td>
<td>8.489 (97%)</td>
<td>3E-3</td>
<td>9.010</td>
</tr>
<tr>
<td>1600</td>
<td>12,932,918</td>
<td>4,443,053 (88%)</td>
<td>11.653 (98%)</td>
<td>3E-3</td>
<td>12.601</td>
</tr>
</tbody>
</table>

Table 3  Same as Table 2, but for 1D periodic systems

<table>
<thead>
<tr>
<th>$N$</th>
<th># Samples</th>
<th># States (%)</th>
<th>$S$ (%)HOMFLY</th>
<th>$\sigma(S)$</th>
<th>$S_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>16,000,080</td>
<td>667 (99%)</td>
<td>0.888 (99%)</td>
<td>3E-4</td>
<td>0.888</td>
</tr>
<tr>
<td>200</td>
<td>32,000,160</td>
<td>29,948</td>
<td>2.165 (100%)</td>
<td>5E-4</td>
<td>2.166</td>
</tr>
<tr>
<td>300</td>
<td>47,942,214</td>
<td>347,488</td>
<td>3.692 (99%)</td>
<td>6E-4</td>
<td>3.705</td>
</tr>
<tr>
<td>400</td>
<td>41,308,708</td>
<td>1,475,414</td>
<td>5.181 (100%)</td>
<td>1E-3</td>
<td>5.562</td>
</tr>
<tr>
<td>500</td>
<td>14,326,942</td>
<td>1,442,183</td>
<td>7.300 (99%)</td>
<td>2E-3</td>
<td>7.474</td>
</tr>
<tr>
<td>600</td>
<td>18,618,306</td>
<td>3,472,365</td>
<td>9.159 (90%)</td>
<td>2E-3</td>
<td>9.479</td>
</tr>
<tr>
<td>700</td>
<td>31,777,950</td>
<td>8,703,710</td>
<td>10.920 (100%)</td>
<td>2E-3</td>
<td>11.387</td>
</tr>
</tbody>
</table>

Table 4  Same as Table 2, but for 2D periodic systems

<table>
<thead>
<tr>
<th>$N$</th>
<th># Samples</th>
<th># States (%)</th>
<th>$S$ (%)HOMFLY</th>
<th>$\sigma(S)$</th>
<th>$S_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>9,100,104</td>
<td>3,839</td>
<td>1.443 (99%)</td>
<td>7E-4</td>
<td>1.443</td>
</tr>
<tr>
<td>200</td>
<td>31,998,021</td>
<td>244,240</td>
<td>3.896 (99%)</td>
<td>8E-4</td>
<td>3.908</td>
</tr>
<tr>
<td>300</td>
<td>44,612,057</td>
<td>2,280,152</td>
<td>6.875 (100%)</td>
<td>2E-3</td>
<td>6.964</td>
</tr>
<tr>
<td>400</td>
<td>33,006,598</td>
<td>5,133,312</td>
<td>9.597 (100%)</td>
<td>2E-3</td>
<td>9.868</td>
</tr>
<tr>
<td>500</td>
<td>25,921,280</td>
<td>7,130,729</td>
<td>11.473 (99%)</td>
<td>2E-3</td>
<td>11.953</td>
</tr>
</tbody>
</table>
The results in the tables show that our sample sets are sufficiently large that this source of error in $S_t$ is very small.

The second source of statistical error results from accessible rare knots that are missed completely in a finite sample. Of course we cannot easily increase the sample size, but we can investigate this source of error by decreasing the sample size, by taking only a fraction $1/s$ of the total states to compute $S_t$. As the sample size becomes smaller, more rare states are missed, which leads to a systematic dependence of the estimated $S_t$ on sample size. If the observed dependence is smooth, we can hope to extrapolate to infinite sample size.

A representative result is shown in Fig. 21, which plots the entropy $S_t$ versus $s$ for $N = 500$ under 2D periodic boundary condition (note the expanded ordinate scale). The abscissa is the number of subsets $s$, so $1/s$ is the fraction of the original set of states in each subset. Here $s = 1$ means the entire sample set is used; $s = 0$ is the limit of an infinite sample set. The plotted values are the average of the entropies computed from the $s$ subsets. The error bars, barely visible on this scale, are the variation between subsets.

Fig. 21 suggests the entropy $S_t$ computed from the full set of states for this ring is not fully sampled, and thus underestimated (for shorter rings, the underestimates are much less pronounced). To extrapolate to limit of an infinite sample size,

$$
\sigma^2(S) = \frac{1}{N_s} \sum_i (1 + \log p_i)^2 p_i (1 - p_i).
$$

The empirical form

$$
S_e(N) = \frac{3}{2} N_{e}^{1/2} + b N_{e},
$$

is still growing with $N_{e}$ for $N_{e}$ up to 1600, so extracting a value of $N_{e}$ from these data alone is problematic.

To extract the entanglement length $N_{e}$ using eqn (3) for finite $N$, the best approach is to equate the limiting slope of $S_t(N)$ to $(3/2)/N_{e}$, assuming we have taken $N$ large enough that the entropy has begun to grow linearly with $N$. It is evident from Fig. 22 that for our aperiodic results, the slope $dS_t/dN$ is still growing with $N$ even for $N$ up to 1600, so extracting a value of $N_{e}$ from these data alone is problematic.

Fig. 22 Ring length dependence of topological entropies, for the aperiodic, 1D, and 2D periodic boundary conditions.
less severe for periodic knots, because the generalized Jones polynomial has additional degrees of freedom in the values of the wrapping indices, which multiply the possible values the invariant may take. We note that up to 90% of our knots in 2D periodic boundary conditions in fact contain periodic components.

The picture is much brighter for our results in periodic boundary conditions, where the dependence of $S_t$ on $N$ is much more nearly linear (and for smaller $N$), suggesting that periodicity indeed helps in reaching the asymptotic limit. The slopes of the two data sets evidently differ (unless we were so bold as to take the slope for the 2D case from the last two points!), but not dramatically. More results over a broader range of $N$ would clearly be helpful, but our algorithm for identifying the entanglement states becomes prohibitively slow very quickly as $N$ is increased further.

To bracket a range for the entanglement length using the results for 1D and 2D cases, we infer values for $S_e$ from the dashed slopes of Fig. 22. Using eqn (3), we obtain $N_{e, 1D} = 1.5 \Delta N/\Delta S = 76$ and $N_{e, 2D} = 52$. Both results are quite close to the estimates for $N_e$ ($67 \pm 10$ or $62 \pm 7$) based on the heuristic chain-shrinking approach (see section 5.1).

6 Summary and discussion

In this work, we have predicted the entanglement length $N_e$ of a polymer melt from purely topological information; namely, the statistics of topological states.

To do this, we have simulated a single long ring, topologically equilibrated under melt conditions, as a proxy for an entangled melt of long chains. A melt of long entangled rings has a local structure indistinguishable from a melt of long entangled linear chains, while at the same time having a well-defined topological state. We chose to study a melt comprising a single ring to minimize finite-length effects for a given total number of monomers, and because topological states correspond to knots rather than links between multiple chains.

We obtain a topologically equilibrated melt of entangled rings by using molecular dynamics together with Monte Carlo moves that allow the chains to cross, while preserving chain connectivity before and after the crossing. This preserves local melt packing structure and identity of rings while sampling topologically distinct states.

We determine the topological state by use of the Jones polynomial invariant from knot theory. We gathered extensive statistics on the probability $p_i$ with which the system is found in knotted state $i$. From this we can compute the topological entropy $S_t$, defined as the information-theoretic entropy of the $\{p_i\}$, namely

$$S_t = -\sum p_i \log p_i.$$

The topological entropy $S_t$ is connected to the chain entanglement length $N_e$ in the limit of long chains by the simple relation

$$S_t = (3/2)N/N_e.$$

The linear dependence on $N$ is expected for long chains because $S_t$ is extensive. Intuitively, we may say that for a given ring length, the shorter is $N_e$, the more different knots the system can tie. For the model we studied (similar but not identical to fully flexible model of Kremer and Grest), we find $N_e = 64 \pm 12$, quite consistent with values obtained from heuristic chain-shrinking methods.

The Jones polynomial is a good but not perfect knot identifier (sometimes giving the same result for distinct knots). Thus our simulation results give lower bounds for $S_t$. Investigations with better but less convenient knot identifiers (HOMFLY polynomial) suggest the resulting systematic errors are small.

As an alternative to the connection between $S_t$ and $N_e$, we also propose a relation between $N_e$ and the probability $P(\alpha)$ that a topologically equilibrated melt comprising a ring of length $N$ is an unknot; namely, that $P(\alpha N_e) = C$ for some well-chosen constant $C$ (or equivalently, that $P(\alpha N_e) = 1/2$ for some constant $\alpha$). The intuitive idea here is that for chains much shorter than $N_e$ we almost always find an unknot, while for chains much longer than $N_e$ we almost never find an unknot. It is much easier to gather good statistics for the unknot probability than for the full topological probability distribution, so this alternative prescription is simpler to compute. Also, the Jones polynomial is believed to be a perfect identifier of unknots, so no systematic errors are made.

A key ingredient of our success in connecting topological entropy to $N_e$ is our use of rings simulated in 1D and 2D periodic boundary conditions, together with our use of the Jones polynomial generalized to periodic crossing diagrams. Periodic boundary conditions mitigate the strong effect on entanglement of closed surfaces, through which the system cannot entangle. With periodic boundary conditions, we reach the limit of $S_t$ depending linearly on ring length for much shorter chains.

Likewise, efficient algorithms for evaluating the Jones polynomial are essential. We simplify the ring configurations before projecting to a crossing diagram by using a modified Kroger algorithm to straighten the chains thereby removing spurious crossings. Also, we simplify crossing diagrams wherever possible by using Reidemeister type 1 and 2 moves to remove spurious twists and recrossings.

The heart of our algorithm for computing the Jones polynomial is the recursive use of the skein relation to remove the shortest subloop of a crossing diagram, in the process generating simpler crossing diagrams to which the same method can be applied.

For periodic boundary conditions our algorithm must be generalized: when no suitable subloop can be found for simplification, the bracket expansion is applied to some crossing in the diagram. Also, for knots in periodic boundary conditions, we account for the invariance of the topological state with respect to the choice of unit cell, by introducing a canonical form for the wrapping indices of the generalized Jones polynomial. Roughly speaking, this corresponds to rotational invariance of the topological state for aperiodic systems.

In future work, we shall test our topological predictions for $N_e$ by varying the stiffness or bulkiness of the chains in our system. For example, we can make our chains stiffer by introducing a three bead bond potential, and simulate a bulkier chain by adding sidegroups or simply lowering the density.

The Lin-Noolandi ansatz well represents the variation in $N_e$ that results from changes in chain stiffness or bulkiness of real polymers, so we know roughly what to expect as we change system parameters. From eqn (20), the topological entropy for chains of varying stiffness and bulkiness should be a function only of reduced chain length $\tilde{N}$ defined as $\tilde{N} = \beta N b^2$, which is the same as $BN/N_e$.
A Equivalence of bracket expansion and skein relation

We first show that the polynomial \( V(a) \) obtained using the bracket summation is consistent with the skein relation, eqn (14). Consider three diagrams that differ by one crossing, as shown in Fig. 7. We denote diagrams \( K_a \) and \( K_b \) stripped of orientations by \( \tilde{K}_a \) and \( \tilde{K}_b \) respectively. Applying the bracket expansion to them, we get \( f_{K_a} = a f_{K_b} + a^{-1} f_{K_b} \) and \( f_{K_b} = a^2 f_{K_b} + a f_{K_a} \), where \( K_a \) and \( K_b \) are defined from \( K + \) or \( K_+ \) as in Fig. 9. Thus we have

\[
a f_{K_b} - a^{-1} f_{K_a} = (a^2 - a^{-2}) f_{K_b}.
\]

Now we notice that \( w_{K_a} = w_{K_b} + 1 \) and \( w_{K_a} = w_{K_b} - 1 \) and that the diagram \( K_b \) can be oriented to get \( K_0 \). Writing \( f \) in terms of \( V \) using eqn (14) and substituting them and the writhe relations into eqn (23), we obtain exactly eqn (10).

Next we explain why orienting the crossing diagrams derived from bracket expansions is arbitrary, and that this arbitrariness does not affect the final results on the Jones polynomial. We use the trefoil as an example, the result of a single bracket expansion does not affect the final results on the Jones polynomial. We use \( \tilde{K}_0 \) and minimize the quadratic sum by twisting or untwisting the trefoil along the meridional and azimuthal direction on the torus diagram. It is known that the matrices

\[
S \equiv \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}
\]

and \( T_x \) generate \( SL_2(\mathbb{Z}) \): every element in the group can be expanded as the products of powers of \( T_x \) and \( S \). Since \( S \) can be written as \( T_x^{-1}T_yT_x^{-1} \), the elements \( T_x, T_y \) and their inverses also generate \( SL_2(\mathbb{Z}) \). This suggests that we can explore the elements in \( SL_2(\mathbb{Z}) \) by building up products of these four elementary matrices raised to certain powers.

Our algorithm of minimizing eqn (19) is based on the recursive application of \( T_x, T_x^{-1}, T_y, \) and \( T_y^{-1} \), and mimics the congruent gradient method in spirit. For a set of wrapping indices \( \{v_i\} \), we first minimize the quadratic sum of wrapping indices by twisting or untwisting the unit cell along the \( y \) axis. This is achieved by applying the family of matrices

\[
M_x(s) = T_y^s = \begin{pmatrix} 1 & s \\ 0 & 1 \end{pmatrix}, \quad s \in \mathbb{Z}
\]

to the vector set, and minimizing eqn (19). By explicitly multiplying \( M_x(s) \) with \( v_i \), it is straightforward to show that eqn (19) is quadratic in \( s \), with a positive quadratic coefficient. So a solution \( s = s_0 \) that minimizes eqn (19) always exists (at most doubly degenerate). Then we take this solution as the new starting point, and minimize the quadratic sum by twisting or untwisting the unit cell along the \( x \) axis, which corresponds the minimization with respect to the family of matrices

\[
M_y(s) = T_x^s = \begin{pmatrix} 1 & 0 \\ s & 1 \end{pmatrix}, \quad s \in \mathbb{Z}.
\]
We recursively apply these two minimization steps, until the solution does not change any more. The set of vectors found from the final solution is used as the canonical form.

In our study, when collecting the histogram for the entangled states, we need to compare both the Jones polynomial and the canonical form of wrapping indices. Since the canonical form may be degenerate, we need to keep track of all the degenerate forms found. We prepare the list of degenerate forms based on two variation steps: (1) rotate the unit cell by $\pi/4$, to switch the role of $x$ and $y$; (2) perturb one minimized solution by $M_x(\pm 1)$ or $M_y(\pm 1)$. The chance of degeneracy decreases with the number of vectors involved, since the degeneracy is normally associated with some kind of symmetry.

Acknowledgements

We thank Andrew Belmonte and Alexei Likhtman for helpful conversations, and NSF DMR-0907370 and CBET-1067554, and ACS-PRF 49964-ND7 for support.

Notes and References

31 The software package is hosted at http://www.cems.umn.edu/research/morse/code/simpatico/home.php.
33 Conventionally, $\pi \equiv a–\pi$ is used as the argument to $V$, here we stick to a to make the relation between skein relation and bracket expansion more transparent, and to avoid using fractions in actual calculations.