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# Entanglements in polymers: I. Annealed probability for loops

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**Abstract.** The effect of the preservation of the topology of the entanglement in systems of polymer loops is investigated. We define a simple two-state linking invariant for a pair of loop polymer chains and show its relationship to the familiar Gaussian linking number. The probability of linking two disjoint sets chosen from a dense melt of closed-loop chains is determined. We discuss the form of the resulting probability and the approximations necessary in obtaining it.

## 1. Introduction

The intuitive physical picture concerning the topology of a system of polymers is understood through the connectivity of the molecules. Each molecule forms an (ideally) unbreakable line, such that the changes in configuration of the polymer never permit an interruption of the backbone during any reconfiguration. Therefore, it is required of a formalism incorporating this, that the dynamical picture with the hard-body interaction amongst the chains and the concept of the permanently connected chain are implemented together. Dynamically two long chains can require a long time to switch places, and in certain situations this time essentially becomes infinite. Such situations are normally dealt with by using the concept of reptation [1–4]—the idea that each polymer moves along a tube caused by the geometrical constraints imposed by the remainder of the molecules, where reconfigurations of the system occur by cooperative motions of the tube and the contained polymer. Where there are loops permanently embedded by and into the substance, which may, in turn, be interlaced by other loops, the dynamics are determined by the fact that the mutual escape of loops is impossible. For the case when there are long free-ended polymers such as tree polymers, structures may have long 'branches' where reptation can only occur by retraction of complete arms and their subsequent extensions (see e.g. [5, 6]) which will greatly extend the time for such a process to occur and hence the viscosity of such a solution. On short timescales such branches may be considered as entangled with the remainder of the polymer system.

However, in the case of polymer network structures the mathematics of dynamical or non-equilibrium treatments becomes too intricate and the necessary simplifications all but remove the essentials one wishes to include [7, 8]. It would be easier to model entanglement and hard-core repulsion effects in the light of equilibrium statistical mechanics. Some treatments of networks do consider excluded volume and the crosslinking, but still compute the results for phantom molecules (see, e.g. [9, 10]). The excluded volume interaction is computed by the weighting of all configurations *a priori*, such that the true topological invariance is lost. (Here the use of the word 'topology' is limited to its geometrical sense as related to the existence of links of physical knots.) It is requisite to include an additional constraining factor in the

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integrand for the partition function to maintain the invariance of the topology of the whole network explicitly.

One approach beyond the phantom limit is in the slipping link model of entanglements (Ball *et al* [11]). Highly dense knotted regions of one polymer strand which have captured (during formation) another strand in their midsts are regarded as localizing two strands in question at a point which is free to slide between crosslinks of the underlying network. The elastic role of the slipping links is due to the effects of their slipping along the molecules of the network as this is stretched, and the molecules themselves becoming ever longer due to their nature as random walks. Other approaches have been made by Rostiashvili *et al* [12, 13] and a recent review has appeared by Kholodenko and Vilgis [14].

As concerns a general topological approach, two problems are immediately at hand. Only truly closed loops lead to a true topological invariant, since equilibrium statistical mechanics does not occupy itself with the timescale of reconfigurations. If the network formation were modelled by the instantaneous crosslinking of strands in a melt, the difficult theoretical question would remain as to identify explicitly the loops thus formed even before the topological implications of such loops can be considered. The problem of timescales may be addressed by the inclusion or consideration or estimation of effective links, above which the timescale of retraction and reconfiguration would become experimentally unfeasible or temporally unrealizable.

In this paper we introduce the concepts of invariance of the topology of polymer systems. Previously implemented methods of incorporating such invariance to the polymer problem as well as introducing knots in a general manner have already been mentioned. Subsequent sections concern themselves with the definition of an intuitively appealing realization of topological classification. This and related definitions are shown to be true topological invariants for two-component links. The invariant is then implemented for systems of ring melts in the annealed case. The quenched cases where such rings can be crosslinked or form a so-called olympic gel is left to the next paper [15] (referred to as II hereafter), after we have introduced the necessary concepts here.

The following two subsections introduce invariants. The second section introduces concepts we require for the calculation of properties due to pairwise, two-state linking invariance. The final section is devoted to the computation of the probability that two sets of chosen polymer chain loops chosen from a dense system are entangled. We find that the result depends upon a parameter expressing the volume fraction occupied by the pairs of rings and produces intuitive results.

### *1.1. Topological invariance*

The second problem lies in the manner of the precise implementation of these constraints upon the topology of the network. The order of linking needs to be identified. Self-linking of any ring represents the lowest; then there are all pairs of links which have pairwise linking constraints. At third order, situations such as the occurrence of Borromean rings play a role, where pairwise rings are not entangled, yet a set of more than two loops is inseparable. The reader is referred to figure 1 for an example of a triplet of such loops.

The methods developed by knot theorists for the classification of links usually rely on the projection of any knot into a plane such that no two crossings occur above each other in the projection. The crossings are then individually labelled and polynomial invariants defined for the various links based upon the orientation of each link and the explicit manner of labelling these crossings. One of the simplest and the oldest of these polynomial invariants is the Alexander polynomial of which a description is given by Wiegel [16]. The nature of statistical

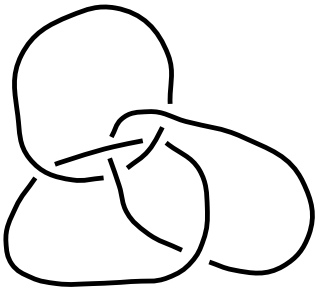

**Figure 1.** Borromean rings are only entangled here as a triplet but have pairwise winding numbers equal to zero.

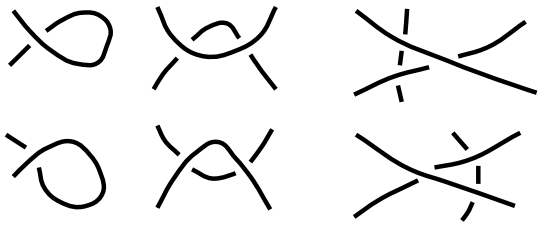

**Figure 2.** The Reidemeister moves relevant to the invariance of pairs of links. The moves of types I, II and III appear in sequence from left to right. Invariance under all three types of moves is said to be of ambient isotopy, while invariance restricted to types II and III is described as regular isotopy.

physics which requires analytical expressions depending on the link constituent paths makes it unfeasible to implement such 'mechanical' procedures of knot classification.

Let an invariant, $I_c$, describing the topological state for some set of configurations be found. The set of loops has to stay in exactly those same configurations which do not alter $I_c$, thus subdividing the system in topological equivalence classes. This does not preclude that schemes of classification of states of links do not have a unique realization. We write,

$$\text{constraint} = \delta(I_{\text{reference}} - I_{\text{test}}). \tag{1.1}$$

$I_c$ may be any complicated functional depending on the precise paths of all the molecules.

Topological invariants for knots and links of arbitrary order are generally tested under the Reidemeister moves, expressions of local permitted reconfigurations of knots [17]. The moves were shown, in a theorem by Reidemeister, to be necessary and sufficient for the topological equivalence of the two-dimensional projection of the embedding of any knot in three-dimensional space. The moves are depicted in figure 2. Invariance under moves labelled I, II and III is described as invariance of ambient isotopy and moves of the types II and III only as regular isotopy. The invariance means that taking any set of links and subjecting the space in which they are embedded to an arbitrary continuous and invertible deformation leaves the topology of the knot invariant. This is a nonlocal property of any such system.

The concepts of formulating the geometry of knots in terms of Hamiltonian and Lagrangian formalisms is reviewed by Atiyah [18]. The role of gauges in physical situations which require non-simply connected spaces has been tackled by several authors, and has motivated some of the analytical expressions used for invariance (see, for example, the treatment of Kleinert for topological structures in superfluids and other condensed matter systems, [19–21]). Edwards [22,23] has also shown that the Gauss invariant can be implemented as an interacting magnetic vector field. Analytic forms of invariants are deducible from Chern–Simons theories [24–26] which seem the most promising candidates for an optimal and complete theory of topological classification [27]. Anyon statistics, and Laughlin wavefunctions (e.g. in [28]) have been employed in attempts at understanding entanglement, in maps to the one-component Coulomb plasma (Kholodenko [29]).

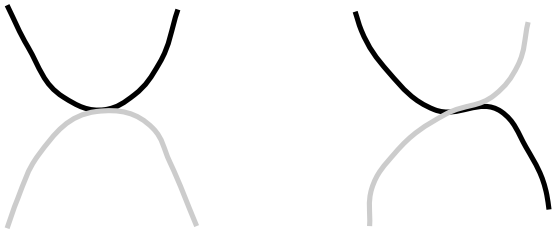

**Figure 3.** A glancing crossing which turns back and a glancing crossing which does indeed cross. The first is not counted by the invariant (equation (1.3)), while the second is. The usual knot projections avoid such ambiguous situations.

### *1.2. Realizations of invariants*

Some analytic forms of invariants such as the Gauss and Arf invariants can be given explicitly. The Gaussian or winding number for paths $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ is given by:

$$4\pi I_{\text{Gauss}}[\boldsymbol{r}_1, \boldsymbol{r}_2] = \oint_1 \oint_2 \frac{\mathrm{d}\boldsymbol{r}_1 \times \mathrm{d}\boldsymbol{r}_2 \cdot (\boldsymbol{r}_1 - \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|^3}. \tag{1.2}$$

The idea that the number of crossings between any two invariant loops can change only by a multiple of two (if glancing crossings are not considered) leads to the basis of an invariant† found by counting the number of intersections between pairs of loops, defined as follows:

$$\begin{aligned} \mathfrak{t}^\star[\boldsymbol{R}_1, \boldsymbol{R}_2]_{\hat{\boldsymbol{x}}} &= \int_{0^+}^{\infty} \mathrm{d}\tau \int_0^L \mathrm{d}s \int_0^{L'} \mathrm{d}s' \, |\hat{\boldsymbol{x}} \cdot (\dot{\boldsymbol{R}}_1(s) \times \dot{\boldsymbol{R}}_2(s'))| \delta^{(3)}(\boldsymbol{R}_1(s) - \boldsymbol{R}_2(s') - \hat{\boldsymbol{x}}\tau) \\ \mathfrak{t}[\boldsymbol{R}_1, \boldsymbol{R}_2]_{\hat{\boldsymbol{x}}} &= \int_{0^+}^{\infty} \mathrm{d}\tau \int_0^L \mathrm{d}s \int_0^{L'} \mathrm{d}s' \, \hat{\boldsymbol{x}} \cdot (\dot{\boldsymbol{R}}_1(s) \times \dot{\boldsymbol{R}}_2(s')) \delta^{(3)}(\boldsymbol{R}_1(s) - \boldsymbol{R}_2(s') - \hat{\boldsymbol{x}}\tau). \end{aligned} \tag{1.3}$$

One loop is being 'pulled' away from the other to infinity in the direction of the *arbitrary* unit vector $\hat{\boldsymbol{x}}$. Alternately, the loops are being projected onto a plane at infinity and the number of mutual crossings are counted. For this reason one can call $\mathfrak{t}$ an extraction invariant. (Appendix A contains invariance proofs and equivalent formal definitions of $\mathfrak{t}^\star$.) The measure in the integral ensures that its result is an integer and that simultaneously the cross-product does not count glancing crossings as those depicted in figure 3 but does those which do indeed cross the line of the other loop. From the above definition, by making use of basic vector identities and the even nature of the Dirac delta function, the observation that the expression

$$\mathfrak{t}[\boldsymbol{R}_1, \boldsymbol{R}_2]_{\hat{\boldsymbol{x}}} = \mathfrak{t}[\boldsymbol{R}_2, \boldsymbol{R}_1]_{-\hat{\boldsymbol{x}}} \tag{1.4}$$

holds is immediate. If the numbers above are true topological invariants of closed loops their values should not depend on the choice of $\hat{\boldsymbol{x}}$.

It is noted that the odd or even nature of the crossing number as defined by equation (1.3) is not affected by the removal of the absolute value in the measure. The absence of this will considerably simplify future statistical mechanical calculations. Henceforth, $\mathfrak{t}$ (note: omission of the asterisk) will be regarded as defined without this. The invariant is then

$$\delta^\star(\mathfrak{t}[\boldsymbol{R}_1, \boldsymbol{R}_2]) = \mathfrak{t}_2[\boldsymbol{R}_1, \boldsymbol{R}_2] = |\mathfrak{t}[\boldsymbol{R}_1, \boldsymbol{R}_2] \bmod 2|. \tag{1.5}$$

The definition of $\delta^\star$ is taken to be,

$$\begin{aligned} &\delta^\star : \mathbb{Z} \to \{0, 1\} \\ &\delta^\star(x) : x \mapsto |x \bmod 2|. \end{aligned} \tag{1.6}$$

† The proof that equation (1.3) defines an invariant modulo two is left to appendix A.

It is now easy to see how this applies to such situations when viewed three dimensionally and that the results above is essentially the same as the Gaussian invariant. We present proof in appendix A. The invariance is definitely broken when the value of $\mathfrak{t}$ changes from odd to even (or vice versa) but the invariant does not distinguish from other topological or geometrical situations. This is the simplest manner of viewing geometrical *inequivalence* of two-links by simply dividing the complete space of possible knottings into two classes. To clarify this point: let two two-link knots with $\mathfrak{t}_1$ and $\mathfrak{t}_2$ be considered. If these integers are both even it is possible that the knots have the same topology. However, if one is odd and the other even any topological equivalence is ruled out. A similar argument holds for a complete system description reduced to pairwise descriptions (the picture in which future considerations will only be made) and as is the case of the implementation of the Gaussian invariant also. This minimal constraint upon the system can provide the lowest estimate of physical effect of entanglement invariance in the replica system. The incorporation of higher numbers of invariance will restrict the free energy of the system to an ever increasing degree.

It is important to note that the calculation of the linking number $I$ or of $\delta^\star$ does not detect all linked states.

## 2. A system of two rings

What is the probability of two rings being formed $\delta^\star$-entangled at a specific density in a melt? When two identical loops of polymer are entangled in the sense of $\delta^\star$-invariance one expects a joint probability distribution of these two rings which differs from the unentangled case.

Constraints which are absolute in the sense that their implementation in a partition function (for example) means that they multiply the remainder of the system by either a one or a zero and cannot be treated perturbatively. There is no parameter related to the constraint in itself which can be treated as small or large with respect to some other quantities, such as is the case for potentials where these two extrema can often be investigated perturbatively. A sensible option for the implementation of an absolute constraint is to treat the constraint variationally or to implement it in an approximate system in which calculations are possible.

Let identical rings of polymer be considered as closed random walks of a given length. We neglect effects of excluded volume. The two-topological invariant can be implemented by considering integral arguments of the cosine:

$$\delta^\star(\mathfrak{t}) = \cos^2\left(\frac{\pi}{2}\mathfrak{t}\right) \tag{2.1}$$

$$= \tfrac{1}{4}\sum_{c=\pm1,0,0} \exp[+\mathrm{i}\pi c\mathfrak{t}]. \tag{2.2}$$

The loop structure follows by writing the closed polymer path functions in terms of Rouse [30] modes,

$$\boldsymbol{r}(s) = \frac{\boldsymbol{r}_0}{\sqrt{N}} + \sqrt{\frac{2}{N}}\sum_{m=-\infty}^{\infty} \boldsymbol{r}_m \exp\left(\frac{2\pi \mathrm{i} m s}{L}\right). \tag{2.3}$$

These contain the periodic nature of the molecule, which is in contradistinction to the case of free ends where expansion occurs in terms of $\cos m\pi s/L$.

### *2.1. Collective coordinates*

Collective coordinates in the context of entanglements have been introduced by Vilgis and Brereton [31], where these were defined depending on the Lagrange multipliers for the pairwise

entanglements. In order to implement replica techniques and to apply the theory to networks, it would be simpler not to include these in a definition.

For a system of $N$ closed paths let the new variables

$$\boldsymbol{u}_i(\boldsymbol{k}) = \int_0^L \mathrm{d}s\, \dot{\boldsymbol{r}}_i(s) \exp(+\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i(s)) \qquad i \in \{1,\ldots,N\} \tag{2.4}$$

be defined. These are the familiar Fourier transformations of the bond-vector density. In terms of these variables the topological invariant may be expressed by:

$$\begin{aligned}\mathfrak{t}[\boldsymbol{r}_i,\boldsymbol{r}_j] &= \frac{1}{(2\pi)^3}\int \mathrm{d}^3k \int_0^\infty \mathrm{d}\tau\, \boldsymbol{u}_i(\boldsymbol{k})\times\boldsymbol{u}_j(-\boldsymbol{k})\cdot\hat{\boldsymbol{p}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{p}}\tau} \\ &= \frac{1}{V}\sum_{\boldsymbol{k}\neq 0}\left(\int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{p}}\tau}\epsilon_{abc}\hat{\boldsymbol{p}}_c\right)u_{ia}(\boldsymbol{k})u_{ib}(-\boldsymbol{k}).\end{aligned} \tag{2.5}$$

$$\mathbb{E}(\boldsymbol{k}) = \int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{p}}\tau}\epsilon_{abc}\hat{\boldsymbol{p}}_c. \tag{2.6}$$

The term in brackets of equation (2.5) will henceforth be denoted by $\mathbb{E}(\boldsymbol{k})$ and plays a crucial role in the characterization of the invariance. Here $\hat{\boldsymbol{p}}$ has been chosen as the unit vector in the direction of the projection. In the case of linking number it is easily found that $\mathbb{E}(\boldsymbol{k}) = \epsilon_{abc}k_c k^{-2}$. After suitable manipulations the relevant parts of an implemented invariant such as $\mathfrak{t}$ lead to the same expression as for the Gaussian. This is in accordance with the results of section 1. We also define:

$$\vec{\Psi}_i(\boldsymbol{k}) = \sum_{j=1}^{M_i}\boldsymbol{u}_j(\boldsymbol{k}) \tag{2.7}$$

such that

$$\begin{aligned}\mathfrak{t}_{ii'} &= \frac{1}{V}\sum_{\boldsymbol{k}}\vec{\Psi}_i\cdot\mathbb{E}\cdot\vec{\Psi}_{i'} \\ &= \sum_{j=1}^{M_i}\sum_{j'=1}^{\tilde{M}_i'}\mathfrak{t}_{jj'}.\end{aligned} \tag{2.8}$$

The number $M_i$ is a macroscopically large number such that the central limit theorem may be applied to $\vec{\Psi}_i$. Therefore, the statistical mechanical Hamiltonian in terms of the Gaussian approximation is suggested. By letting $M_i$ and $\tilde{M}_j$ represent two subsets of the rings in a system it is clear that the strength with which the entanglement constraint holds is less strong in that fewer entanglement events can be distinguished. Nevertheless, the classification of the entangled state is still rigorous under a complete distribution for the collective variables. This is a property of the Boolean-type rules for entanglement invariance as treated in the initial sections.

In the case of the Wiener measure, collective variables such as $\boldsymbol{u}_i$ and $\vec{\Psi}_i$ are poorly defined as the random walk since they are nondifferentiable. However, it is noted that that the above condition ensures that gradients of the walk are not uncorrelated. Problems of this nature can be resolved by introducing stiff, or worm-like walks or by regularizing integrals with cut-offs by noting that the polymer molecules actually consist of a finite number of oriented bonds. The latter is the approach which will be taken here and it is done with the cut-off. We have the condition

$$\int_0^L \mathrm{d}s\, \dot{\boldsymbol{r}}(s) = 0. \tag{2.9}$$

We note that this provides satisfactory results in the view of previous work [22].

*2.2. Further properties*

The inclusion of terms such as $\boldsymbol{u}_i \times \boldsymbol{u}_i$ is not problematical, as the measure ensures a zero contribution (i.e. cross-product of a vector with itself) and the integration over $\tau$ can be taken as being from a very small distance, say a molecular diameter, to infinity. We compute the linking probability for two sets of rings.

The ring-like and chain-like properties restrict the functional forms of variables such as $\boldsymbol{u}(\boldsymbol{k})$ and $\vec{\Psi}(\boldsymbol{k})$ may assume. First, this property yields (see Brereton and Vilgis [31, 32]),

$$\boldsymbol{u}(0) = 0 \tag{2.10}$$

and

$$\boldsymbol{k} \cdot \boldsymbol{u}(\boldsymbol{k}) = 0. \tag{2.11}$$

The latter follows from definite integration of $\partial/\partial s \exp(+\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}(s))$ over $s$ between zero and $L$, and means that the bond-vector density must be divergenceless. There are no 'sources' or 'sinks' of polymer contour for closed molecules. Such terms are sometimes referred to as 'gauge-fixing' in analogy with the Chern–Simons formalisms of knots.

The second condition is that for any suitable open surface $S$, the integral $\int_S \vec{\vartheta} \cdot \mathrm{d}\vec{S} = n$ yields an integer $n$, and where $\vec{\vartheta}$ represents the bond-vector density. This expresses the condition that an integral number of lines pass through any open surface. The analogy here is established to the formalism of the magnetic field which is divergenceless, and describes an Abrikosov lattice of superconductivity in which the magnetic flux is quantized. Here vortices are of the diameter of the polymer. The condition may also be rephrased in such a way that the entanglement of the field of Gaussian distribution must be an integer for a knot with every closed loop or path from or to the infinite boundaries of the box.

An additional property is of note, since it may be applied successfully in the quenched (replica) cases to be discussed later. If the loop described by $\boldsymbol{r}(s)$ were to be subjected to a transformation $\mathbb{T}$ independent of $s$ or $\boldsymbol{r}(s)$ such that,

$$\boldsymbol{R}(s) = \mathbb{T} \cdot \boldsymbol{r}(s) \tag{2.12}$$

then the appropriate bond-vector density Fourier component in terms of the original $\boldsymbol{u}$ would be,

$$\begin{aligned} \boldsymbol{u}_{\mathrm{new}}(\boldsymbol{k}) &= \int_0^L \mathrm{d}s\, \mathbb{T} \cdot \dot{\boldsymbol{r}}(s) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\mathbb{T}\cdot\boldsymbol{r}(s)} \\ &= \mathbb{T} \cdot \boldsymbol{u}(\mathbb{T} \cdot \boldsymbol{k}). \end{aligned} \tag{2.13}$$

The condition that it forms a closed loop remains unaltered as discussed previously.

## 3. Annealed case

For the collective variables defined previously it is possible to derive the probability that two disjoint sets of rings are entangled in a melt of rings for the case of modulo two invariance by extraction. The Gaussian approximation for the two-ring variables is derived in appendix B. In addition to the Gaussian approximation the constraints upon the $\vec{\Psi}_1$ and $\vec{\Psi}_2$ are imposed that these be ring-like. The probability distribution then changes from

$$P_{\vec{\Psi}}[\vec{\Psi}_1(\boldsymbol{k}), \vec{\Psi}_2(\boldsymbol{k})] = \exp\left(-\frac{1}{2}\operatorname{Tr}\ln\frac{1}{2\pi}\mathbb{A}_{ij}\right)\exp\left(-\frac{1}{2}\sum_{ij}\sum_{\boldsymbol{k}}\vec{\Psi}_i(\boldsymbol{k}) \cdot \mathbb{A}_{ij}^{-1}(\boldsymbol{k}) \cdot \vec{\Psi}_j(\boldsymbol{k})\right) \tag{3.1}$$

where $\mathbb{A}_{ij}^{-1}$ is the Gaussian approximant, to

$$\tilde{P}_{\vec{\Psi}}[\vec{\Psi}_1, \vec{\Psi}_2] = \exp\left(-\frac{1}{2}\,\mathrm{Tr}\ln\frac{1}{2\pi}\mathbb{A}_{ij} + \frac{1}{2}\,\mathrm{Tr}\ln\frac{1}{2\pi}\boldsymbol{k}\cdot\mathbb{A}_{ij}\cdot\boldsymbol{k}\right)$$
$$\times\exp\left(-\frac{1}{2}\sum_{ij}\sum_{\boldsymbol{k}}\vec{\Psi}_i(\boldsymbol{k})\cdot\mathbb{A}_{ij}^{-1}(\boldsymbol{k})\cdot\vec{\Psi}_j(\boldsymbol{k})\right)$$
$$\times\int\mathfrak{D}\phi_1\mathfrak{D}\phi_2\exp\left(+\mathrm{i}\sum_{k}\sum_{i}\phi_i(-\boldsymbol{k})\boldsymbol{k}\cdot\vec{\Psi}_i(\boldsymbol{k})\right). \tag{3.2}$$

The matrices above are both indexed by the Cartesian coordinates and in the ring labels. Here, let the probability that the sum of all entanglement numbers between two sets of $N$ and $N-M$ rings is odd, be denoted as follows:

$$p_{12} = \int\mathfrak{D}\vec{\Psi}_1\mathfrak{D}\vec{\Psi}_2\left\{\tilde{P}_{\vec{\Psi}}\times\tfrac{1}{4}\sum_{\{c\}}\left[\exp+\mathrm{i}\pi c\sum_{\boldsymbol{k}}\vec{\Psi}_1\mathbb{E}\vec{\Psi}_2\right]\right\}\delta_{\mathrm{Int}}\mathcal{N}_{\mathrm{Int}}. \tag{3.3}$$

Here $\delta_{\mathrm{Int}}\mathcal{N}_{\mathrm{Int}}$ represents the constraint that only those contributions in the Gaussian approximation are retained which produce integral entanglement numbers with the appropriate normalization. The expression, $p_{12}$, represents the annealed average of an entanglement, or the probability that a spontaneously created system of rings would be in a topological state as described above. A direct evaluation of the term with the mutual entanglements (without $\delta_{\mathrm{Int}}\mathcal{N}_{\mathrm{Int}}$) above would result in a probability,

$$p_{12,c}\propto\exp[-\tfrac{1}{2}\,\mathrm{Tr}\ln(\mathbf{1}+\mathbb{A}_{ij}\mathbb{E}_{jk})]\exp[+\tfrac{1}{2}\,\mathrm{Tr}\ln\boldsymbol{k}\cdot(\mathbb{A}_{ij}^{-1}+\mathbb{E}_{ij})^{-1}\cdot\boldsymbol{k}]. \tag{3.4}$$

The expression above refers only to those cases where $c=\pm1$, where $c$ enters the expression squared. In the following two sections the two constraints are considered separately.

The condition (2.11) causes the determinant of a rank two matrix in Cartesian space to be computed. Inversion of the matrix between the $\boldsymbol{k}$ can be rather tedious, especially when the matrix has additional replica labels. Only the transverse components of the matrix $\mathbb{A}_{ij}$ play a role as $(\mathbf{1}-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}})\mathbb{A}_{ij}(\mathbf{1}-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}})$ is projected since the ring condition requires that the fields $\vec{\Psi}$ be transverse. The relevant $2\times2$ submatrix can be found by a $\boldsymbol{k}$-dependent rotation of the appropriate matrices in the Cartesian space. Let a rotation of the Cartesian coordinates be defined by:

$$R(\boldsymbol{k}) = \begin{pmatrix}\sin\phi & \cos\phi & 0\\ \cos\vartheta\cos\phi & \cos\vartheta\sin\phi & -\sin\vartheta\\ \sin\vartheta\cos\phi & \sin\vartheta\sin\phi & \cos\vartheta\end{pmatrix} = \begin{pmatrix}\tilde{\boldsymbol{k}}_1\\ \tilde{\boldsymbol{k}}_2\\ \tilde{\boldsymbol{k}}_3\end{pmatrix}. \tag{3.5}$$

The vectors, $\tilde{\boldsymbol{k}}_i$ are orthonormal where specifically $\tilde{\boldsymbol{k}}_3=\hat{\boldsymbol{k}}$. The angles $\vartheta$ and $\phi$ represent the usual angles related to spherical coordinates of $\hat{\boldsymbol{k}}$. The function $\vec{\Psi}$ can now be rewritten as the sum of the transverse components and the one in the direction of $\boldsymbol{k}$: $\vec{\psi}+\hat{\boldsymbol{k}}\zeta$. The ring-condition ensures that $\zeta$ is identically zero for all $\boldsymbol{k}$. Any Gaussian integral over rings is now two dimensional,

$$\int\exp(-\tfrac{1}{2}\vec{\Psi}\mathbb{D}\vec{\Psi}) = \int\exp(-\tfrac{1}{2}\vec{\Psi}R^TR\mathbb{D}R^TR\vec{\Psi})$$
$$= \int\exp(-\tfrac{1}{2}\vec{\psi}\bar{\mathbb{D}}\vec{\psi}) \tag{3.6}$$

such that only the $\tilde{\boldsymbol{k}}_1$ and $\tilde{\boldsymbol{k}}_2$ submatrix of $R\mathbb{D}R^T$ remains, which is denoted by a bar. The notation $\mathbb{G}^T$ represents the transpose of a matrix $\mathbb{G}$. The rotation ensures that any part of the

tensor $\mathbb{D}$ which projects from or into the direction $\hat{\boldsymbol{k}}$ is rotated into the third row or column of $R\mathbb{D}R^T$. In addition it follows that,

$$\bar{\mathbb{E}}(\boldsymbol{k}) = \begin{pmatrix} 0 & \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} \\ -\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} & 0 \end{pmatrix} E(\boldsymbol{k}) \tag{3.7}$$

where

$$E(\boldsymbol{k}) = \int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{p}}\tau}. \tag{3.8}$$

This is seen from the following derivation:

$$\begin{aligned}(R^T\mathbb{E}R)_{ab} &= \sum_{cde} \tilde{\boldsymbol{k}}_{c;e}\epsilon_{cde}\hat{\boldsymbol{p}}_e\tilde{\boldsymbol{k}}_{b;a}E(\boldsymbol{k}) \\ &= \tilde{\boldsymbol{k}}_a \times \tilde{\boldsymbol{k}}_b\cdot\hat{\boldsymbol{p}}\mathbb{E}(\boldsymbol{k}) = \epsilon_{abc}\tilde{\boldsymbol{k}}_c\cdot\hat{\boldsymbol{p}}E(\boldsymbol{k}).\end{aligned} \tag{3.9}$$

The properties of the Levi-Civita symbol, $\epsilon_{abc}$, have been used.

Combining the results of appendix B and the equations above and by neglecting $\delta_{\mathrm{Int}}\mathcal{N}_{\mathrm{Int}}$ here, leads to the result,

$$\langle \mathrm{e}^{+\mathrm{i}\pi c\mathfrak{t}_{12}}\rangle = \exp\left[-\operatorname{Tr}\ln\det\left(\mathbf{1} - \frac{\pi^2c^2M(N-M)}{V^2}\Delta^T\bar{\mathbb{A}}\Delta\bar{\mathbb{A}}\right)\right] \tag{3.10}$$

$$= \exp\left[-\frac{2V}{\pi^2}\left(\frac{6}{\ell L}\right)^{3/2}\int_0^{x_c}\mathrm{d}x\, x^2\ln(1+c^2\varrho^2g^2(x)x^{-2})\right]. \tag{3.11}$$

Here the matrices to which reference is made have already been reduced by the procedure of rotation. It is found that:

$$\Delta = -\frac{2}{\boldsymbol{k}\cdot\hat{\boldsymbol{p}}}\begin{pmatrix} 0 & \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} \\ -\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} & 0 \end{pmatrix} \tag{3.12}$$

and

$$\mathbb{A}(\boldsymbol{k}) = \delta_{ab}f\left(\frac{k^2\ell L}{6}\right). \tag{3.13}$$

The derivation of $f$ is given in appendix B. The parameter appearing above is given by:

$$\varrho^2 = 8\pi^2M(N-M)V^{-2}\left(\frac{\ell L}{3}\right)^3. \tag{3.14}$$

Therefore, $\varrho$ expresses the volume fraction occupied by the polymer chains. We expect that if this parameter is small, spontaneously formed entanglements between rings will be highly unlikely.

The procedure above has revealed the topological properties as expected. The rotational transformations and restrictions and the regrouping into terms such as $\Delta$ have led to an expression for entanglement which is *independent* of the specific choice of direction of projection and is the same as for the Gaussian linking number. Any other result would have rendered the approximation and formalism useless.

We define a periodic function by:

$$2\delta_p(x) = 1 + \sum_{\eta=1}^{\infty} 2\cos\pi\eta x/2. \tag{3.15}$$

Employing a self-consistent condition upon the two entanglement fields in the system, one postulates that $\vec{\Psi}\mathbb{E}\vec{\Psi}'$ must be an integer, where the $\vec{\Psi}$ are computed by the RPA. The

normalization can then be written as:

$$\mathcal{N}^{-1} = \left\langle \tfrac{1}{2} \sum_{\eta=0}^{\infty} \sum_{d=\pm 1} \exp +\mathrm{i}\pi\eta \, \mathrm{d}\mathfrak{t} \right\rangle (2 - \delta_{0\eta})$$

$$= \sum_{\eta=0}^{\infty} \{\exp -\tfrac{1}{2} \operatorname{Tr} \ln(1 + 4\eta^2 \varrho^2 g^2 x^{-2})\}[2 - \delta_{0\eta}]. \tag{3.16}$$

The probability becomes:

$$p_{12} = \mathcal{N} \frac{1}{2} \sum_{\eta=0}^{\infty} \sum_{d=\pm 1} \frac{1}{4} \sum_{\{c\}} \left\{ \exp -\frac{1}{2} \operatorname{Tr} \ln \left( 1 + \left( \eta d + \frac{c}{2} \right)^2 4\varrho^2 g^2 x^{-2} \right) \right\} [2 - \delta_{0\eta}] \tag{3.17}$$

$$= \tfrac{1}{2} + \mathcal{N} \tfrac{1}{8} \sum_{\eta=0}^{\infty} \{\exp -\tfrac{1}{2} \operatorname{Tr} \ln(1 + (\eta + \tfrac{1}{2})^2 4\varrho^2 g^2 x^{-2})$$

$$+ \exp -\tfrac{1}{2} \operatorname{Tr} \ln(1 + (\eta - \tfrac{1}{2})^2 \varrho^2 4 g^2 x^{-2})\}[2 - \delta_{0\eta}]. \tag{3.18}$$

From this expression one also sees that were the replacement $c \to 2c$ to be made in the system, the probability would always be equal to one in accordance with the odd/even nature of the cosine squared test. The replacement would simply entail a multiplication of the appropriate entanglement number by two making the odd/even test trivial. This is true for all even replacements. However, as the expression stands above the sums are not directly computable. In the limit of high densities one can assume that

$$\exp[-\tfrac{1}{2} \operatorname{Tr} \ln(1 + (\eta - \tfrac{1}{2})^2 \varrho^2 g^2 x^{-2})] \sim \exp[-\tfrac{1}{2} \operatorname{Tr} \ln(1 + (\eta)^2 \varrho^2 g^2 x^{-2})]$$

$$\sim \text{small}$$

to first order to give

$$p_{12} \sim \tfrac{1}{2} + \tfrac{1}{2} \exp[-\tfrac{1}{2} \operatorname{Tr} \ln(1 + 4\varrho^2 g^2 x^{-2})] \tag{3.19}$$

as derived already.

## 4. Results and discussion

For loops consisting of a finite number of straight-line bonds there is also a corresponding maximal entanglement number. If one loop has $\mathcal{N}$ bonds and another $\mathcal{N}'$ then the maximum value of an expression of the type of $\mathfrak{t}$ is given by $\mathcal{N} \times \mathcal{N}'/9$. This is based on the fact that the smallest possible loop can be formed by three straight bonds in triangular arrangement.

The finite number of bonds also plays a role when $k^2$ in expression such as equation (B12) is large, which should then be rewritten in its discrete form

$$S = \sum_{ij} \frac{\ell}{3L} \mathbf{1}(\delta_{ij} - 1) \exp \left[ -\ell L k^2 / 6 \left( \frac{i - j}{\mathcal{N}} - \frac{(i - j)^2}{\mathcal{N}^2} \right) \right]. \tag{4.1}$$

The sum reduces to the form of $\sum_{m=0}^{\zeta} a^{m^2}$ which can be approximated by its largest term. Writing $\mathcal{N} = L/\ell_c$ this is the expression for $A(\boldsymbol{k})$ becomes extremely small when $k^2 > 6/\ell\ell_c$ with width proportional to $\frac{6\mathcal{N}}{\ell L k^2}$.

Arguments as to the finite number of bonds in any loop molecule lead to the regularization of integrals by a cut-off

$$k_c^2 = 6x_c^2/\ell L \tag{4.2}$$

and

$$k^2 < k_c^2 = 6/\ell\ell_c. \tag{4.3}$$

That such a cut-off exists can be explained by the fact that the polymer ring consists of a finite number of end-joined linear segments, each of which can maximally only have one crossing with any other segment in a specific projection. The maximum number of crossings is equal to $M(N-M)L^2/9\ell^2$. The integral of equation (3.11) is performed in appendix C. The final result for the probability of an odd number of entanglements in a melt of rings subdivided into two macroscopically large sets is:

$$p_{12} = \frac{1}{2} - \frac{1}{2}\exp\left\{-\frac{2V}{\pi^2}\left(\frac{6}{\ell L}\right)^{3/2}\left[\frac{x_c\varrho^2}{2} - \frac{\varrho^2}{12} + \frac{\pi\varrho^3}{12}\right]\right\} \tag{4.4}$$

to the highest order in $\varrho$ and $k_c$.

The result is valid when the Gaussian approximation holds and where the integrals are still dominated for the cut-off $1 \ll \varrho \ll k_c$. For $\varrho^2$ larger than $(k_c^2/6)\ell L$ the contribution in the exponent diverges giving, as is expected, a value for $p_{12}$ of one half. It can be expected for high densities that in half the cases there is an odd number of entanglements between two macroscopically large disjoint sets. For the opposite limit in the density $p_{12} \simeq 0$, which is also in accordance with expectations.

In our simple approximative scheme we see that if the concentration of loops remains constant, the effect of increasing the chain lengths causes $p_{12}$ to tend to its maximal value. In equation (4.4) it is observed that the behaviour of the probability of entanglement is determined by the concentration of the number of segments squared. This is in accordance with the fact that the we have investigated a single pair of sets under *nonlocal* constraints.

In this paper it is shown that a simple two-state invariant can be defined which is related to the Gauss linking number. The simple annealed case of linking of rings in a dense melt has been investigated, and it has been demonstrated that this simple even/odd entanglement number test is applicable under the random phase approximation (RPA) used for the melt of rings. The results agree with physical intuition. They can now be used to study the effect of entanglements on the properties of gels [15].

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## Appendix A. Invariance proofs

The arguments leading to the invariants of two topological classes as expressed in equation (1.3) contain more detail as to classification of knots than under the modulo two test generally used hereafter. In fact there must be as many distinct knotted states described by the invariant without the absolute value restriction of the integrand as by the Gaussian integral. The value of $\mathfrak{t}$ (without modulo two restrictions) is shown to be closely related to the winding number. It emerges from the intuitive geometrical and projective ideas concerning knots which the counting invariant is designed to recognize.

Only the case of two-component links and no self-linking will be considered to argue that $\mathfrak{t}$ is an invariant. It suffices, therefore, to show invariance under any local reconfigurations of the knots under Reidemeister moves of types II and III. Type I moves apply only to the case of self-knotting which is ignored here. Mathematical uncertainties emerge for the type I case due

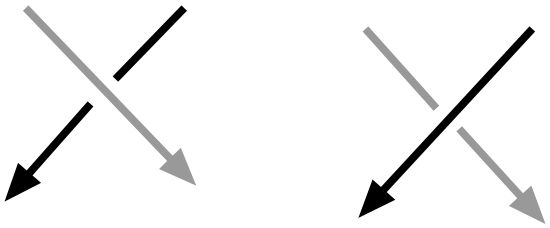

**Figure A1.** The signs of the crossings for directed knots for extraction direction into the plane of the page. The left-hand situation corresponds to a sign $\epsilon = +1$ and the other to the negative case. The sense of rotation from the upper arrow to the lower one, in a right-handed screw manner, establishes the sign.

to the problem of the framing of knots (where certain gauges or procedures have to be chosen for a knot invariant to have meaning).

Let two loops of an ordered link $L$ be denoted by $\alpha$ and $\beta$, such that one writes $L(\alpha, \beta)$. The set of crossings, in some projection, which does not matter here, is written as $\alpha \sqcap \beta$. The linking number is defined by,

$$\mathrm{lk}[L] = \mathrm{lk}(\alpha, \beta) = \tfrac{1}{2} \sum_{p \in \alpha \sqcap \beta} \epsilon(p). \tag{A1}$$

Here $\epsilon(p)$ represents the sign of the crossing, which is illustrated in figure A1 for oriented links, i.e. the parametrization of the loop gives it a sense of direction. It is a standard result that ambient isotopy of links $L_1$ and $L_2$ leads to:

$$\mathrm{lk}[L_1] = \mathrm{lk}[L_2]. \tag{A2}$$

If one denotes the set of all crossings (including self-crossing) by $\mathcal{C}(K)$, the writhe is defined as

$$w(K) = \sum_{p \in \mathcal{C}(K)} \epsilon(p). \tag{A3}$$

The expression defined by 'pulling apart' two loops also concerns crossings. However, only those crossings where a designated loop passes above the other are considered. Signs are still attributed as with $\epsilon$, which is also the role of the cross-product term in the definition of $\mathfrak{t}$. The set of such crossings which is automatically determined by the operations defining $\mathfrak{t}^\star$ will be written as $\alpha \sqcap^\star \beta$, such that,

$$\mathfrak{t}^\star(\alpha, \beta) = \sum_{p \in \alpha \sqcap^\star \beta} |\epsilon(p)|. \tag{A4}$$

**Definition A1.** *Equation (A4) is simply the total number of crossings occurring during an extraction. Furthermore,*

$$\mathfrak{t}(\alpha, \beta) = \sum_{p \in \alpha \sqcap^\star \beta} \epsilon(p). \tag{A5}$$

**Definition A2.** *Expression (A5) can be viewed as alternative definition of the previously introduced quantities*†. *The analogue to the writhe could also be defined in terms of the 'action of separation' as taking each part of the link path separately and moving it along the vector $\hat{\boldsymbol{x}}$ and by counting appropriately.*

**Proposition A1.** *Given any link $L$ with parametrizable component link paths, the quantities $\delta^\star(\mathfrak{t}^\star[L])$ and $\delta^\star(\mathfrak{t}[L])$ are invariants of ambient isotopy.*

† Clearly, $\alpha \sqcap^\star \beta = \beta \sqcap^\star \alpha$ is not true.

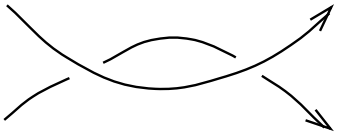

**Figure A2.** A type II crossing with reference to proposition 4.2.

**Proof.** The function $\delta^\star$ tests whether the argument contained is odd or even, returning a value of either zero or one, respectively. The normalization in the measure of the analytical expression for $\mathfrak{t}^\star$ ensures that it has either the values zero or one at each instance of crossing by extraction. For the $\mathfrak{t}$ it is clear from the definition that an instance of crossing by extraction, say $\{s, s', \tau\} \in \alpha \sqcap^\star \beta$, $\epsilon(p) = |\epsilon(p)| = 0$ always if the sign of the crossing is zero. Then the sums forming $\mathfrak{t}$ and $\mathfrak{t}^\star$ must have the same nature, i.e. evenness or oddness.

Say that the knot is changed locally only by a type II move. This always entails either two crossings, not of value zero, or no crossings by extraction at all (depending on which strand lies above the other relative to the direction of extraction). Any change in the sums comprising both $\mathfrak{t}$ and $\mathfrak{t}^\star$ must therefore be $\pm 2$ or 0.

Say that the knot is changed locally by a move of type III. Only two-links are being investigated, and consequently, the strands must be labelled, such that either one or two are extracted, and self-crossings ignored (as the whole of one member of the link is being translated). Again it is clear that any changes can only be even in number. □

Testing for even or odd, nonetheless, does not do the definition $\mathfrak{t}(\alpha, \beta)$ any justice, as it does contain more detail. If a type II crossing were being considered the sign of the crossing by extraction on the left of figure A2 would have a value +1, and the other would be assigned $-1$. The sum of these two then results in a difference of *zero*. The following proposition formalizes the idea.

**Proposition A2.** *Given any link $L$ with parametrizable component link paths, $\mathfrak{t}[L]$ is an invariant of ambient isotopy.*

**Proof.** The theorem is proved by making use of the fact that the change in $\mathfrak{t}$ under moves of type II and of type III is zero.

There are two crossings by extraction in any Reidemeister II knot alteration. The lines can be straightened according to Jordan's theorem, such that in a 2D graph, the upper (as regards direction of extraction) forms a straight line on the $x$-axis. Along the $y$-axis follows the line continuous, differentiable line with non-zero derivatives at points $a$ and $b$. These are the only two crossings of the $x$-axis by definition of the Reidemeister moves and operative crossings. Hence, from fundamental analysis the derivatives at a and b exist and are of opposite sign. These signs correspond to the extraction crossing signs and prove the first part of the proposition.

The proof for type III moves simply entails the remark that the *sliding* of a crossing does not change its sign. □

**Proposition A3.** *For any two-component link $L = \{\alpha, \beta\}$ where $(\alpha \sqcap^\star \beta) \cap (\beta \sqcap^\star \alpha) = \emptyset$ the expression $\mathfrak{t}(\alpha, \beta) + \mathfrak{t}(\beta, \alpha)$ is even and equals twice the linking number.*

**Proof.**

$$\mathfrak{t}(\alpha, \beta) + \mathfrak{t}(\beta, \alpha) = \sum_{p \in \alpha \sqcap^\star \beta} \epsilon(p) + \sum_{p \in \beta \sqcap^\star \alpha} \epsilon(p)$$

$$
\begin{aligned}
&= \sum_{p\in(\alpha\sqcap^\star\beta)\cup(\beta\sqcap^\star\alpha)} \epsilon(p) \\
&= \sum_{p\in\alpha\sqcap\beta} \epsilon(p) \\
&= 2\ \mathrm{lk}(\alpha,\beta) \qquad \text{(A6)}
\end{aligned}
$$

$\mathrm{lk}(\alpha,\beta)\in\mathbb{Z}$. □

**Corollary A1.** *For any two-component link,* $\mathfrak{t}(\alpha,\beta)$ *is odd (even) iff* $\mathfrak{t}(\beta,\alpha)$ *is odd (even).*

This simple observation will provide a basis for the definition of collective coordinates in a statistical mechanical system, subjected to invariance of the form modulo two. It is also remarked here the operation of 'switching' the two loops in a two-component link by changing the set under investigation $\alpha\sqcap^\star\beta\leftrightarrow\beta\sqcap^\star\alpha$ is also equivalent to a transformation $\hat{\boldsymbol{x}}\leftrightarrow-\hat{\boldsymbol{x}}$ in addition to changing the labels inside the definition of the analytically defined invariant.

By now enhancing the definition of the set $\alpha\sqcap^\star\beta$, such that the hitherto used $\alpha\sqcap^\star\beta$ is denoted by, $\alpha\sqcap^\star_+\beta$, but that the projections underneath, i.e. by moving the first knot downwards are written as $\alpha\sqcap^\star_-\beta$. This is simply a change in the integration over $\tau$ in equation (1.3). From this additional definition and equation (1.4), as well as the property that bringing a ring from infinity and pulling it through the other to negative infinity must have a total of zero (line 2), the following deduction ensues:

$$
\begin{aligned}
&\mathfrak{t}_+(\alpha,\beta)=\mathfrak{t}_-(\beta,\alpha) \\
&\mathfrak{t}_+(\alpha,\beta)-\mathfrak{t}_+(\beta,\alpha)=0 \qquad \text{(A7)} \\
&\mathfrak{t}(\alpha,\beta)=+\mathfrak{t}(\beta,\alpha)
\end{aligned}
$$

establishing the close association of this formalism with that of the linking number. Later this will be confirmed directly when, upon integration, the functional form of the implemented invariants is identical. However, it is re-emphasised that $\mathfrak{t}(\alpha,\beta)$ cannot be defined sensibly for a self-knot.

## Appendix B. Collective coordinates

It is useful to transform the coordinates which arise naturally from the modulo two entanglement invariance formulation into collective coordinates as given in equation (2.7). The RPA for these as free noninteracting rings is computed in this appendix.

### *B.1. Definitions*

The parametrized delta function of the transformation gives,

$$
\begin{aligned}
\int\left\{\prod\mathfrak{D}\boldsymbol{r}_i\mathfrak{D}\vec{\phi}_i\right\}\exp\Bigg[&-\frac{3}{2\ell}\sum_i\int\mathrm{d}s\,\dot{\boldsymbol{r}}_i^2(s)+\mathrm{i}\sum_{i\boldsymbol{k}}\vec{\phi}_i(\boldsymbol{k})\cdot\vec{\Psi}_i(\boldsymbol{k}) \\
&-\mathrm{i}\sum_{i\boldsymbol{k}}\vec{\phi}_i(\boldsymbol{k})\cdot\sum_j\int\mathrm{d}s\,\dot{\boldsymbol{r}}_j(s)\mathrm{e}^{+\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j(s)}\Bigg] \\
\simeq\int\left\{\prod\mathfrak{D}\vec{\phi}_i\right\}&\\
\times\exp\Bigg\{&-\frac{1}{2}N\Bigg\langle\iint\mathrm{d}s\,\mathrm{d}s'\sum_{\boldsymbol{k}ii'}\vec{\phi}_i(\boldsymbol{k})\cdot\dot{\boldsymbol{r}}(s)\dot{\boldsymbol{r}}(s')\cdot\vec{\phi}_{i'}(-\boldsymbol{k})\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}(s)-\boldsymbol{r}(s'))}\Bigg\rangle
\end{aligned}
$$

$$+\mathrm{i}\sum_{ik}\vec{\phi}_i(\boldsymbol{k})\cdot\vec{\Psi}_i(\boldsymbol{k})\Bigg\} \tag{B1}$$

in order to express the new Gaussian distribution, $P_{\vec{\Psi}}$ as,

$$P_{\vec{\Psi}}[\vec{\Psi}_1(\boldsymbol{k}),\vec{\Psi}_2(\boldsymbol{k})] = \exp\left(-\frac{1}{2}\,\mathrm{Tr}\ln\frac{1}{2\pi}\mathbb{A}_{ij}\right) \times\exp\left(-\frac{1}{2V}\sum_{ij}\sum_{\boldsymbol{k}}\vec{\Psi}_i(\boldsymbol{k})\cdot\mathbb{A}^{-1}_{ij}(\boldsymbol{k})\cdot\vec{\Psi}_j(\boldsymbol{k})\right). \tag{B2}$$

Here the angular brackets denote the average over the free system in the Wiener measure for a polymer.

The definitions below are introduced:

$$\mathbb{A}_{ij}(\boldsymbol{k}) = \begin{pmatrix}\mathbb{A}_1(\boldsymbol{k}) & 0\\ 0 & \mathbb{A}_2(\boldsymbol{k})\end{pmatrix} \tag{B3}$$

$$\mathbb{A}_1(\boldsymbol{k}) = \frac{M}{V}\mathbb{A}(\boldsymbol{k}) \tag{B4}$$

$$\mathbb{A}_2(\boldsymbol{k}) = \frac{N-M}{V}\mathbb{A}(\boldsymbol{k}) \tag{B5}$$

$$\mathbb{A}(\boldsymbol{k}) = \left\langle\int_0^L\int_0^L \mathrm{d}s\,\mathrm{d}s'\,\dot{\boldsymbol{r}}(s)\dot{\boldsymbol{r}}(s')\mathrm{e}^{+\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}(s)-\boldsymbol{r}(s'))}\right\rangle. \tag{B6}$$

The average may be performed in terms of bond vectors, which are constrained to form a closed molecule, as performed by Brereton and Vilgis [32], or, as is done here in terms of the Rouse modes relevant to such a molecule, in which no additional delta functions are required. Integrating over these variables will be of particular use later for systems with localized polymer paths.

The value of $\mathbb{A}$ then follows, by using a generating function, taking derivatives, and by writing the polymer variable, $\boldsymbol{r}$, in terms of equation (2.3):

$$G[\boldsymbol{J}(s),\boldsymbol{k}] = \mathcal{N}\int\prod_m \mathrm{d}r_m\,\exp\left\{\frac{-3L}{2\ell}\sum_m\left(\frac{2\pi m}{L}\right)^2\boldsymbol{r}_m\cdot\boldsymbol{r}_{-m} +\mathrm{i}\boldsymbol{k}\cdot\sum_m\boldsymbol{r}_m(\mathrm{e}^{2\pi\mathrm{i}ms/L}-\mathrm{e}^{2\pi\mathrm{i}ms'/L}) + \mathrm{i}\sum_m\int_0^L\mathrm{d}s\,\boldsymbol{J}(s)\cdot\boldsymbol{r}_m\left(\frac{2\pi m}{L}\right)\mathrm{e}^{2\pi\mathrm{i}ms/L}\right\}. \tag{B7}$$

Then the well-established procedure leads to the appropriate function. It is noted here that the use of a random walk without stiffness constraints leads to complications at points on the walk where $|s-s'|$ becomes small. Where these complications occur it is helpful to revert to the expression for the bond-vector density as derived for a finite number of bond vectors, and in particular to the contribution in $\boldsymbol{kk}$.

$$\mathbb{A}(\boldsymbol{k}) = \int_0^L\int_0^L\mathrm{d}s\,\mathrm{d}s'\left[\frac{\partial^2}{\partial\boldsymbol{J}(s)\partial\boldsymbol{J}(s')}\frac{G[\boldsymbol{J},\boldsymbol{k}]}{G[0,0]}\right]_{J=0}. \tag{B8}$$

Taking the derivatives with respect to the arguments of the generating function and setting their values as zero results in the expression for $\mathbb{A}$,

$$\mathbb{A} = \iint\mathrm{d}s\,\mathrm{d}s'\left\{\frac{\ell^2}{9}\boldsymbol{kk}\frac{(s-s')}{L}\left[1-\frac{|s-s'|}{L}\right]+\frac{\ell}{3L}\mathbf{1}[L\delta(s-s')-1]\right\} \times\exp\left[-\frac{\ell Lk^2}{6}\left(\frac{|s-s'|}{L}-\frac{(s-s')^2}{L^2}\right)\right]. \tag{B9}$$

This has the correct symmetries of the ring.

The result consequently has the form,

$$\mathbb{A}(\boldsymbol{k}) = f(\boldsymbol{k})\mathbf{1} + g(\boldsymbol{k})\hat{\boldsymbol{k}}\hat{\boldsymbol{k}} \tag{B10}$$

which is easily inverted in the Cartesian space:

$$\mathbb{A}^{-1}(\boldsymbol{k}) = f^{-1}(\boldsymbol{k})\mathbf{1} + \frac{f^{-1}(\boldsymbol{k})g(\boldsymbol{k})}{f(\boldsymbol{k}) + g(\boldsymbol{k})}\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}. \tag{B11}$$

*B.2. Simplification and approximation*

The arguments and integrals over $s$ and $s'$ nevertheless make the expression as it stands rather complicated in an analytical treatment. Furthermore, the discussion in the main text refers to the additional ring constraint which removes the dependence on components of the collective variables, $\vec{\Psi}$, perpendicular to the vector $\boldsymbol{k}$. It is then feasible to approximate the result using the dominant contribution (this has been successfully used elsewhere; see e.g. [31].), which provides the true $\mathbb{A}$ without the term in $\boldsymbol{kk}$, as is required. A bond-vector approach to this average produces a function which is odd around $L/2$ in the interval $[0, L]$:

$$\begin{aligned}\mathbb{A}(\boldsymbol{k}) &= \int_0^L \int_0^L \mathrm{d}s\,\mathrm{d}s'\,\langle \dot{\boldsymbol{r}}(s)\dot{\boldsymbol{r}}(s')\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}(s)-\boldsymbol{r}(s'))}\rangle \\ &= \int_0^L \int_0^L \mathrm{d}s\,\mathrm{d}s'\,\mathbf{1}\left(\frac{\ell}{3L}\right)(L\delta(s-s') - 1) \\ &\quad \times \mathrm{e}^{-\ell k^2(|s-s'| - \frac{|s-s'|^2}{L})/6} + \text{irrelevant terms } \boldsymbol{kk} \qquad \text{(B12)} \\ &\simeq \int_0^L \int_0^L \mathrm{d}s\,\mathrm{d}s'\,\langle \dot{\boldsymbol{r}}\dot{\boldsymbol{r}}\rangle\langle \mathrm{e}^{+\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}\rangle. \qquad \text{(B13)}\end{aligned}$$

The dominant contribution, (B13), is (B12) without the unnecessary terms. This differs from the usual integrals which give rise to the Debye function due to the quadratic dependence on arc-difference in the exponent of equation (B9), the form which follows from the ring condition, containing the symmetry of the separations established by $|s-s'| \leftrightarrow L - |s-s'|$.

By separating the scalar contribution to

$$\mathbb{A} = \mathbf{1}A = \delta_{ab} f\left(\frac{k^2\ell L}{6}\right) \tag{B14}$$

equation (B12) may be transformed into the form,

$$\frac{3L}{\ell}A(\boldsymbol{k}) = L^2 - 2L^2\mathrm{e}^{-k^2\ell L/24}\int_0^{1/2}\mathrm{d}y\,\exp\left(+\frac{k^2\ell L}{6}y^2\right). \tag{B15}$$

This integral provides difficulties for further analysis unless it is simplified. A similar situation occurs in the calculation of the structure factor of free chains which gives rise to the Debye function. This (Debye) function is frequently approximated by a rational function which satisfies the limiting behaviour of the Debye function. The approximation is accurate to within 15% everywhere over the range [6].

The limiting behaviour for small and large wavevector, where the definition

$$\kappa^2 = \frac{k^2\ell L}{6} = k^2 R_{\mathrm{g}}^2 \tag{B16}$$

is made can be determined from (B12). For $\kappa^2/4 \ll 1$ one finds that

$$\frac{3L}{\ell}\left(A - L^2\frac{\ell}{3L}\right) = -2L^2\left(\frac{1}{2} - \frac{\kappa^2}{12} + \cdots\right) \tag{B17}$$

and in the opposite extreme which is obtained when the rings are regarded as very long the expression

$$A \simeq \frac{\ell}{3L}\left(L^2 - \frac{2L^2}{\kappa^2}\right) \tag{B18}$$

may be derived directly from equation (B15). Approximate corrections to the latter equation follow from a redefinition of integration variables which give the integral whose upper bound (for large $\kappa$) may be approximated by infinity enabling the development of a series of gamma functions.

$$\begin{aligned}\frac{3L}{\ell}(-L^2\frac{\ell}{3L} + A) &= -\frac{2L^2}{\kappa^2}\int_0^{\kappa^2/4} \mathrm{d}g\,(1-4g\kappa^{-2})^{-1/2}\mathrm{e}^{-g} \\ &\simeq -\frac{2L^2}{\kappa^2}\int_0^{\infty} \mathrm{d}g\left(1+\frac{2g}{\kappa^2}+\cdots\right)\mathrm{e}^{-g} \qquad \text{(B19)} \\ &= -\frac{2L^2}{\kappa^2} - \frac{4L^2}{\kappa^4} + \cdots. \qquad \text{(B20)}\end{aligned}$$

In determining the integrals over the wavevector of expressions such as above, it frequently becomes important to consider the case where the polymer is of finite stiffness or even wormlike for derivatives of the polymer path of its arc-length to exist. Finite loop stiffness has been modelled by a cut-off length, or by softened interactions, or may be resolved by renormalization techniques.

## Appendix C. Fourier space integrals

It is necessary to perform the sum or integration over the Fourier components of the logarithm of the function which emerges from the determinants in the main text.

$$\begin{aligned}I &= -\sum_{k>0}\ln\left[1+\frac{\pi^2 M(N-M)}{V^2}\left(\frac{4\ell L}{3}\right)^2\frac{1}{k^2}f^2\left(\frac{k^2\ell L}{6}\right)\right] \\ &= -\frac{V}{\pi^2}\int_0^{\infty}\mathrm{d}k\,k^2\ln\left(1+\varrho^2\frac{6}{k^2\ell L}f^2\left(\frac{k^2\ell L}{6}\right)\right).\end{aligned} \tag{C1}$$

Here it is assumed that $1 \ll \varrho^2 \ll 6k_c^2/\ell L$ which is the large $k$ cut-off. This cut-off has to since the fact that there is only a finite number of linear bonds in the ring thus restricting the maximal crossing number. The integral is performed by transforming to a new variable $x = k\sqrt{\frac{\ell L}{6}}$, and $f$ is given by,

$$f(x) = 1 - 2\mathrm{e}^{-x^2/4}\int_0^{\frac{1}{2}}\mathrm{d}y\mathrm{e}^{+x^2y^2}. \tag{C2}$$

In order to perform the integral above it is important to understand the asymptotic behaviour of the integrand. Elsewhere it has been derived that

$$\frac{f^2(x)}{x^2} \sim \begin{cases} x^2/36 + \mathcal{O}(x^4) & \text{small } x \\ x^{-2} + 4x^{-4} + \mathcal{O}(x^{-6}) & \text{large } x. \end{cases} \tag{C3}$$

Integration by parts then leads to,

$$\begin{aligned}I &= \frac{x^3}{3}\ln[1+c^2\varrho^2 f^2 x^{-2}]_0^{x_c} - \int_0^2 \mathrm{d}x\,\frac{x^3}{3}\frac{\varrho^2\frac{\partial}{\partial x}\frac{f^2}{x^2}}{1+\varrho^2 f^2 x^{-2}} - \int_2^{x_c}\mathrm{d}x\,\frac{x^3}{3}\frac{\varrho^2\frac{\partial}{\partial x}\frac{f^2}{x^2}}{1+\varrho^2 f^2 x^{-2}} \\ &= a_0 + a_1 + a_2.\end{aligned} \tag{C4}$$

Consequently, one has

$$a_0 = \frac{x^3}{3}\ln\left(1+\rho^2\frac{f^2(x)}{x^2}\right)\Bigg|_0^{x_c} \simeq \frac{\varrho^2}{3}\left\{x_c + \frac{8+\varrho^2}{2x_c} + \mathcal{O}(\varrho^4/x_c^3)\right\}. \tag{C5}$$

It has been assumed here that $\frac{1}{2} \ll \rho^2 \ll x_c^2$. However, as $\varrho \sim x_c$ it is found that the terms above gives a contribution proportional to $\frac{1}{3}x_c^3 \ln 2$.

So it is found that,

$$a_1 = \int_0^2 \mathrm{d}x\, \frac{x^3}{3}\frac{\varrho^2\partial/\partial x(f^2(x)x^{-2})}{1+\varrho^2 f^2(x)x^{-2}} \sim \mathcal{O}(\varrho^{-1}) \tag{C6}$$

which is a small correction for high densities. The integral for large $k$ gives up to the highest orders in $\varrho$ and the cut-off:

$$\int_2^{x_c} \mathrm{d}x\, \frac{x^3}{3}\frac{\varrho^2\partial/\partial x f^2(x)x^{-2}}{1+\varrho^2 x^{-2}f^2(x)} \simeq -\varrho^2 x_c/6 + \varrho^2/12 - \varrho^3\pi/12. \tag{C7}$$

This is the result as presented in the main text. An alternative approach to performing the integration lies in identifying the divergent contribution, subtracting it in the integrand and estimating the non-divergent correction to $I$.

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