ACADEMIC
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Analysis of trapped entanglements in polymer networks

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Abstract

This work reviews different standard methods to analyze trapped entanglements of polymer networks and discusses their advantages and drawbacks with respect to simplicity, computing time and accuracy of the results. Since this standard analysis is based on the pairwise test of closed cycles, two algorithms for the determination of these cycles are introduced and compared. The decomposition into meshes creates unsolved problems regarding the non-ambiguity and the completeness of the received results. Examples are given in order to show their effects and to start further discussion to receive more convenient methods. As one possible solution Vassiliev's invariants are discussed and an approximation method is introduced to correct the possible multiple counting of entanglements.
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Keywords: Trapped entanglement; Polymer network; Gaussian linking number; Alexander-Polynomial; HOMFLY-Polynomial; Vassiliev; Invariants; Decomposition; Cycles; Algorithm

1. Introduction

The description of the elastic behavior of a polymer network is still a fundamental field of research in polymer physics. Since the 1930s different basic theories [1–4] were developed to understand the exceptional ability of polymers to permit reversible deformations up to a multiple of the initial length. Over the years scientists recognized that the topology of the networks influences their deformation behavior and they started to consider more and more accurate models as the constraint junction theory [5,7,8], the slip-link model [9,10], the constrained chain model [11,12] or many others [13–15,18]... including characteristics of the topology of the treated networks. At the same time several important new algorithms were discovered in the field of knot theory, which allow a relatively comfortable and accurate description of the topology of a number of closed cycles and are now applied in different fields of modern physics [30,54]. Since the determination of entanglements at molecular level was not possible with experimental methods, it became a topic of computational research [17–22]. Due to the great progress in technology, extension of computa-

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tional resources and development of new simulation techniques it is now possible to create sufficiently large networks and to analyze the evolving structure using modern mathematics.

One point of great interest is still the determination of the number and type of trapped entanglements and their theoretical treatment and description. To simplify complex statistics of different detected entanglements one has to consider the elastic behavior of permanent entangled chains. Transverse stretching of the sample in Fig. 1 results in the formation of a "physical cross-link" at the intersection of the two meshes. In contrast to the fixed chemical cross-links the physical cross-links are able to slip along the chains during the deformation and may change their position for the next deformation. But nevertheless they are trapped and their number is fixed unless any mesh is destroyed.

In general it is not very difficult to see how two discrete meshes entangle, but it is almost impossible to count the right number of physical cross-links as part of a network. The reason is that most meshes share chains with other meshes. These shared chains lead to multiple counting of the same entanglement. Furthermore the entanglement cannot be fixed at one chain due to its mobility along the mesh. For profound investigations on the effect of physical cross-links during the deformation process of a polymer network and their comparability to chemical cross-links it is necessary to determine the accurate number of these physical cross-links and to determine their behavior during deformation.

Due to the problem mentioned above this work introduces a new method for approximative calculation of the number of physical cross-links. Knowing the increasing complexity of the topology shown in simulations of single polymeric rings [40,42] or entangled systems [22,44] and differences in accuracy, simplicity or computing time of algorithms used, this work gives a brief review of useful algorithms to select the most convenient method. Since there is no definite rule, two algorithms for subdivision of networks into meshes are compared concerning applicability and accuracy of the resulting outcome. Furthermore examples are given for entanglements which cannot be detected using any method of previous analysis of polymer networks [17–22]. Therefore more convenient and general methods have to be developed to detect entanglements in networks. As possible solution for some of theses problems Vassiliev's invariants are introduced. At the end of this article we will give a short outline of required properties of more general methods to solve the problems discussed.

Before we start with our discussions we give a short relationship between the mathematical and physical terminologies used. The polymer networks or parts of networks can be interpreted as spatial graphs. The chains of a network correspond to the edges of a graph as well as the cross-links to the vertices. Any mesh of the physical network can be treated as constituent knot in the spatial graph and therefore the term trapped entanglement corresponds to non-trivial constituent links in the graph. The definition of physical
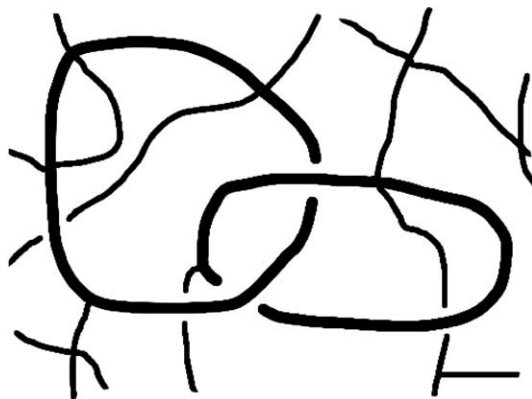

Fig. 1. Two meshes forming one physical cross-link as part of a chemical cross-linked network.

cross-links cannot be translated directly, because a constituent link in the graph can form more than one physical link depending on its topology.

2. Methods for the determination of trapped entanglements

Every currently used method for the determination of entanglements is based on the pairwise analysis of closed cycles without any common chemical cross-link. Polynomial invariants are not restricted to this pairwise analysis and can be extended to any number of cycles. Although it is known that there should exist many entanglements of closed cycles consisting of more than two chains which cannot be detected by pairwise analysis [2] the treatment of such cases has begun recently. However their effects seem to be negligible for systems consisting of small rings [22]. If one starts to analyze a simulated network, it is a great advantage to check for spatial overlap and for common chemical cross-links to save computing time. When periodic boundary conditions are used one has to check the validity [3] of the closed cycles (in networks often called meshes) [35,36]. Note that the computation time can be reduced using Michels simplification method [34]. For example, using the bond-fluctuation-method, first introduced in [46], one can eliminate a single segment of one chain if its predecessor and its successor can be connected by the shortest existing bond.

2.1. Gaussian linking number

At the end of the 1960s Edwards [6,16] started to use the Gaussian linking number (GLN) for a better description of entanglements and topology of single polymer chains. The GLN is defined as

$$G = \frac{1}{4\pi} \oint_{w_1} \oint_{w_2} \frac{(\mathrm{d}\vec{r_1} \times \mathrm{d}\vec{r_2}) \cdot (\vec{r_1} - \vec{r_2})}{|\vec{r_1} - \vec{r_2}|^3}, \tag{1}$$

whereby w_i and w_j denote the closed cycles and $\vec{r_1}$ and $\vec{r_2}$ the position vectors along the components of the entanglement. The GLN describes the numbers of pairwise windings of the two cycles tested, disregarding the windings of one component with itself. This fact causes errors in the detection of entanglements. For example, consider the Whitehead-link [4] 5_1^2 in Fig. 2, which is the simplest undetectable link, but is one of the three simplest links altogether. Michels and Wiegel [27] showed in their systematic study of the GLN and the Alexander-Polynomial that 29 of the 91 simplest entanglements cannot be detected using the GLN. However, the analysis of networks consisting of short subchains, which form relatively short meshes, shows that the GLN is a reasonable approximation. On the other hand one has to be careful, if the percentage of entanglements which have a GLN greater than one is not negligible. Another disadvantage of this method is the lacking determination of the type of entanglement. However, the GLN is still the most commonly used way for the description of trapped entanglements in literature [17–21] due to its simple implementation using common integration routines.

2.2. Determination of entanglements using knot theory

The following two methods are based on the analysis of regular two-dimensional projections of entanglements. In simulations – as in nature – every mesh consists of three-dimensional arranged molecules

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[2] For example, consider all Brunnian links not being entangled pairwise but being entangled as a whole [29].

[3] Cycles are no artifact of the boundary conditions.

[4] The number in the center denotes the minimum possible number of crossings of the entanglement, the superscript counts the components of the entanglement and the subscript numbers different entanglements having the same number of crossings.
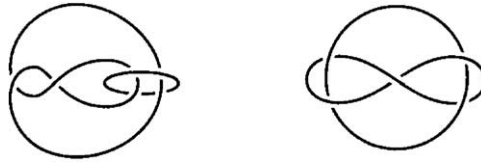
Fig. 2. Two different projections of the Whitehead-link showing the absence of pairwise windings.

linked by bonds, which can be pictured as set of points and straight lines. To get a regular projection of this set on a two-dimensional plane one has to assure that no point is projected onto a line not directly connected to that point or onto any other point of the mesh. To save computing time, one can project the entanglement several times and choose the simplest projection. This is very important for the analysis of complex systems using the HOMFLY-Polynomial, whose computing time can be doubled increasing the number of crossings by one [29].

2.2.1. Alexander-Polynomial

The Alexander-Polynomial was first introduced in 1928 as algebraic invariant to characterize knots and links of chains [23]. After it was shown by Conway [24] that only two rules are sufficient for the calculation of the Alexander-Polynomial $\triangle$, two algorithms were published by Vologodskii and coworkers [25,26] to compute the polynomial by solving determinants determined by the regular projection. [5] It is defined recursively by the following two equations:

$$\triangle(\bigcirc) = 1 \tag{2}$$

and

$$\triangle(L_+) - \triangle(L_-) + (t^{1/2} - t^{-1/2})\triangle(L_0) = 0, \tag{3}$$

whereby L_+, L_- and L_0 denote the same link except for one previously chosen crossing being of the type pictured in Fig. 3 and whereby $\bigcirc$ denotes the unknot. The above equations allow the determination of a knot. Links consisting of n components need a modified calculation as described in [26] resulting in an Alexander-Polynomial depending on n variables. There are some interesting features of this polynomial, which can be used for fast detection of two linked meshes. It is known [26] that the GLN and the Alexander-Polynomial of any two-component link are connected by the equation

$$|G| = \triangle(1,1). \tag{4}$$

As Michels and Wiegel [27] pointed out, any two-component link consisting of less than 10 crossings can be distinguished from an unlinked system by the use of two simple criteria: first check if the GLN equals zero, and secondly check if the following equation is valid:

$$\triangle(-1,-1) = 0. \tag{5}$$

The trivial link (two unlinked meshes) is the only link consisting of less than 10 crossing which satisfies both. Unfortunately an unique classification of the type of the polynomials is not possible, because only 82 different polynomials exist for the 91 simplest links. But it is a convenient way to detect whether two meshes are linked or not, when the links have less than 10 crossings.

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[5] The second publication contains an obvious misprint; the correct version is: case (1b) Type II: $a_{kk} = -s$.
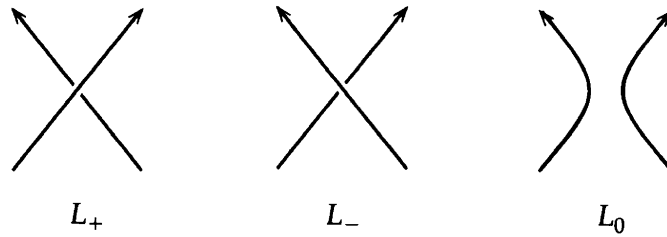
Fig. 3. Types of crossings.

Note that the alteration of one but not all arbitrarily chosen circuiting directions or the inverting of one but not all components could change the polynomials [29]. For a table which describes links complete up to nine crossings see [45].

2.2.2. HOMFLY-Polynomial

The HOMFLY-Polynomial was first introduced in 1985 by Freyd et al. [28] and is until now the most exact possibility for the determination of links. This polynomial permits an one to one assignment for the 91 simplest links consisting of less than 10 crossings [45]. If one wants to detect knots, there are 246 polynomials for the 250 simplest prime knots having less then 11 crossings, which also means an almost one to one assignment. [6] For a more general comparison of the polynomials see [53]. This polynomial is defined analogous by two equations [29,30]:

$$P(\bigcirc) = 1, \tag{6}$$

$$lP(L_+) + l^{-1}P(L_-) + mP(L_0) = 0. \tag{7}$$

In 1999, Gouesbet et al. [31,32] published an algorithm to classify the HOMFLY-Polynomial of knots or links of arbitrary number of components. Note that there are just few tables in literature, mostly incomplete regarding all possible forms of polynomials. The best choice is still [45], being complete up to nine crossings.

Recapitulating the above review it can be stated that there exist three different possibilities for detection of pairwise entanglements of closed cycles which should be chosen in consideration of the accuracy of the results claimed. For simple systems of short meshes the GLN suffices for the description of entanglements. If one wants to know more exactly, if two meshes are entangled, the Alexander-Polynomial should be chosen. But if one wants to obtain results concerning the different types of entanglements or knots, the HOMFLY-Polynomial is the best choice. However, it can be possible that the calculation of the HOM-FLY-Polynomial transcends the resources for computing time.

3. Decomposition of random networks into meshes and resulting problems

The spatial randomness of polymer networks implies a distribution of size [43] and an arbitrary arrangement of meshes. In this case the first step of topological analysis consists of the determination of one set of meshes describing the whole network and adapting it for a valid analysis of trapped entanglements. As Franzblau [36] pointed out algorithms using the ''shortest path'' criterion are qualified for this decomposition, because it makes no sense to analyze any long and complicated path through the whole

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[6] The Alexander-Polynomial, which offers 222 different polynomial for the 275 simplest prime and non-prime knots [33], is not as accurate as the HOMFLY-Polynomial.

system, which can be expressed as a combination of shorter meshes. Due to a lack of well-defined rules for the decomposition of random networks, there exists a number of algorithms. We will introduce two of them which fit best for this problem.

The method of Franzblau [36] determines irreducible meshes using the "shortest path" criterion. Starting with the minimum possible length of the meshes the maximum length of the meshes which are included in the search is extended as long as each part of any closed path is part of a mesh determined. The resulting set of meshes is set without ambiguity with regard to their length, but the total number of meshes needed cannot be specified at the beginning of the search. The method of Lang et al. [37] starts with the fixed minimum number of meshes also using the "shortest path" criterion and using a spanning tree to determine and to optimize the length of the meshes searched. This fixed minimum number of meshes is equivalent to the cycle rank used in several theories of polymer networks [38]. For further discussion of these two algorithms, we have to consider a few facts, which can lead to remarkable errors when using the improper one of these algorithms, or increase computing time noticeably.

Independent of the method for decomposition, one finds most of the chains being used several times as part of any mesh. For example, look at the left part of Fig. 4 consisting of chains 1–3. These chains form not less than two meshes consisting of two chains. Therefore at least one of the chains 1–3 is more than once part of a mesh.

The distribution for the number of uses, when decomposing unimodal networks [7] using our algorithm, is shown in Fig. 5. For a detailed information regarding the networks see [39], for further information regarding the special form of the distributions see [35]. There is a significant difference concerning the number of uses for the two presented algorithms depending on the structure of the networks, because Franzblau's method detects more meshes than needed and uses therefore most chains more often. However, the important two factors that should be kept in mind are: there is a distribution for the uses of chains in meshes and there is no well defined rule for the decomposition.

Considering Fig. 4, a different number of entanglements is found depending on the algorithm chosen. When each chain is of the same length, Franzblau detects three meshes in the left part (chains 1–3) whereas our algorithm detects two. But there are three possibilities for forming these two meshes in the second case of this model network: the mesh consisting of chains 1 and 2 (called mesh A), the mesh with 1 and 3 (B), or the mesh with 2 and 3 (C). Depending on the set of meshes chosen and on the algorithm one finds a different number of entanglements: Franzblau detects the Hopf-link 2_1^2 two times, our algorithm detects two 2_1^2 in the case (B)–(C) and one 2_1^2 otherwise. In Fig. 4 there is one physical link between the left and the right part of the system and our analysis of the entanglement should give this result independent of the meshes chosen.

There are cases, where the non-ambiguity and the completeness of the results are not ensured. First we will take a look at the non-ambiguity of the results obtained and we will show that there is no possibility to exactly identify physical links in the network. For this purpose, look at Fig. 6. The meshes consisting of chains 1 and 3 (A) or consisting of chains 2 and 3 (B) form a link of type 2_1^2 with chain 4. The mesh (C) of chains 1 and 2 forms the 4_1^2-link with the right part. When one does not know the whole structure but just knows the entanglement of meshes (A) and (B) and the chains which form the meshes, one could assume that there exists just one entanglement, situated at chain 3 (cf. Fig. 4). Therefore the counting of physical links is ambiguous and the information, which chain is part of which mesh is not allowed to be used for the determination of physical links as long as the structure of the whole network is not known. But this is really impossible due to the size of the simulated networks. Additionally the type of the entanglements detected is determined by the set of meshes. If mesh (C) is not part of the decomposition, the 4_1^2-link cannot be detected.

The completeness of the results cannot be ensured because there are cases which cannot be detected by analysis of the meshes formed by chemical cross-links and chains between. In Fig. 7 the chains 1–4 and the

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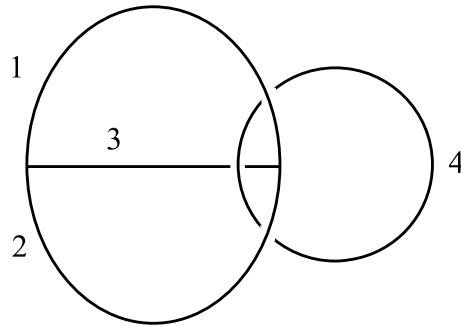[7] Networks consisting of subchains of equal length.

Fig. 4. An ambiguous decomposition creates errors in counting physical cross-links.
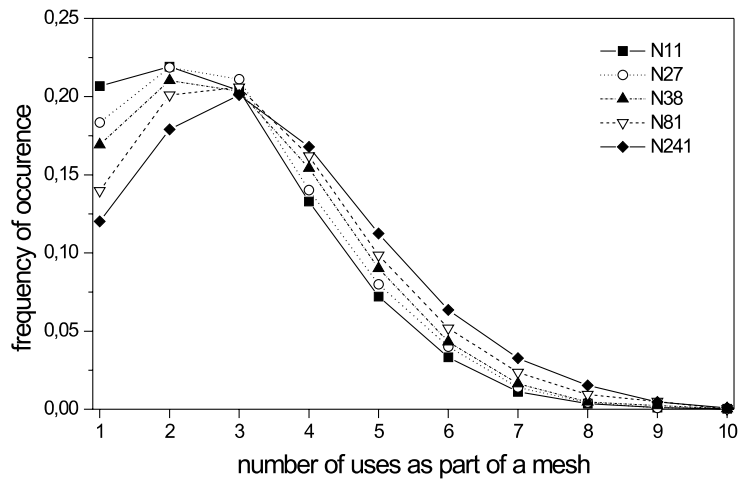

Fig. 5. Number of uses as part of a mesh for the chains of unimodal networks. The denomination N11 stands for: N, unimodal network; 11, 11 segments between cross-links.
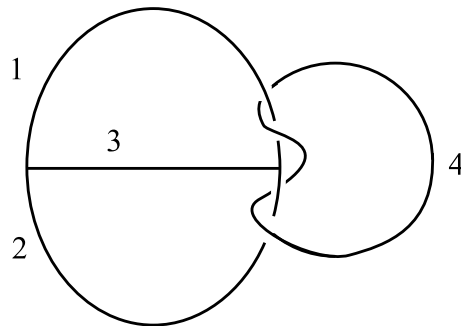

Fig. 6. Example for the ambiguity in identifying physical links.

meshes (A) and (B) form together an ''additional'' mesh which cannot be detected without the knowledge of the entanglement between meshes (A) and (B). Hence the additional mesh is not detected by decomposing the network, no entanglements of chain 4 can be found, which is not part of any other mesh formed only by
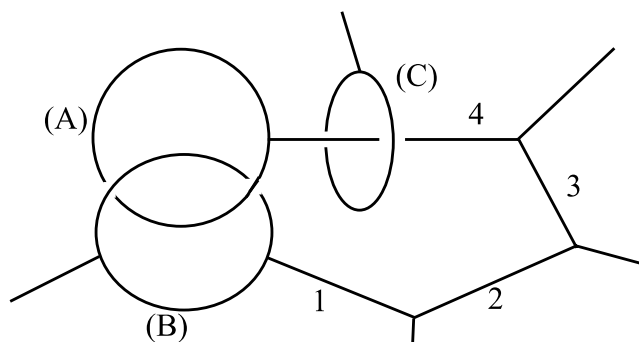
Fig. 7. Sketch of a network showing that entanglement can form additional meshes and that entanglement of additional meshes cannot be detected by pairwise analysis of standard meshes. All chains with no number lead to other parts of the network.

chemical cross-links and chains between. Note that it is not possible to introduce an additional chemical cross-link between the meshes (A) and (B) for better analysis without changing the topology of the network. If there is a third chain or mesh temporarily entangled with meshes (A) or (B), this temporary entanglement can get trapped by introducing this link. Therefore it is not permitted to change the network in some way or another for analysis.

The above example is not very important for networks at high conversion, where nearly every chain is part of a mesh. But in the vicinity of the gel-point most chains are not part of a mesh. Hence, an analysis of entanglements based on pairwise tests of meshes yields an underestimation of the real value. Given that mesh (C) in Fig. 7 and all chains attached to it are not part of the gel-component in terms of the classical treatment, the size of the gel-component will be underestimated. Equally each trapped entanglement of any mesh which is not part of the gel-component, leads to a further underestimation. Brunnian links of any type fortify this independent of the extent of reaction. For a valid determination of the sol–gel transition all that cases have to be considered. But they are still disregarded in theoretical treatments, without knowing their real influence.
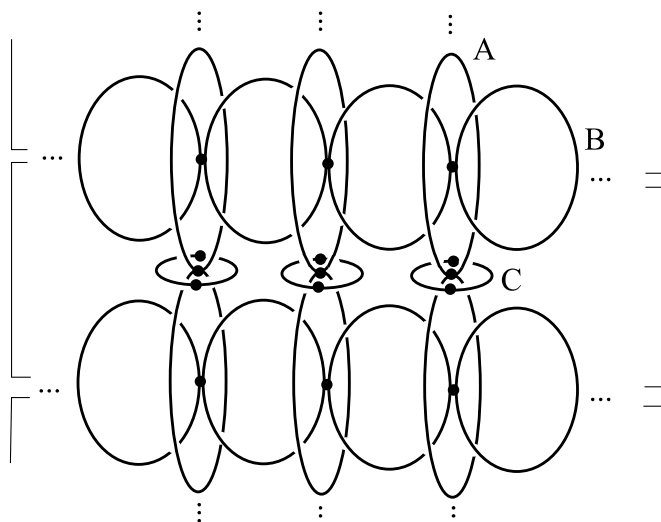

Fig. 8. Sketch of a part of a network mostly composed of entanglement that cannot be detected. Points denote cross-links, lines denote chains, the brackets at the right and at the left symbolize 2_1^2 links at the end of each row.

As a deterrent example look at Fig. 8. The meshes of type (A) are continued vertically, the meshes of type (B) are continued horizontally and the meshes (C) are continued perpendicular to (A) and (B) and there is a huge number of (A)s, (B)s and (C)s parallel to each row forming a big cuboid of meshes. There are no trapped entanglements between any of these meshes. If the first (B)s form the 2_1^2-link with their neighboring first (B)s and the last (B)s do the same, the collectivity of all loops forms a network. Decomposition of this collectivity would result in a huge number of components not forming a network by classical theory even though each chain is part of a mesh and every cross-link connects four chains. Even if one knows that all the chains form a network, one just can detect the entanglements at the end of the (B)-rows, still not able to detect the structure of the network.

Since the amount of the cases of non-detectable entanglements cannot be determined until now we have to confine our analysis to the detectable entanglements. Therefore we introduce an approximation method for the determination of the number of physical cross-links concerning pairwise analysis of closed cycles for further discussion and further improvement of the analysis. This approximation should be valid at high extents of reaction.

4. Approximation method for the determination of the number of physical cross-links

First we will recapitulate some facts: we have to confine our analysis to the detectable entanglements. As indicated above the multiple use of chains as part of different meshes causes errors in counting physical cross-links. The information which chain is part of which mesh is not allowed to be used for the determination of physical links unless the structure of the whole network is known. This is impossible for networks of usual size. The determination of entanglements is not complete and not unique. The determination of the meshes itself is also not unique for random systems.

Due to this problems and inaccuracies we introduce the following procedure:

1. Decompose the chosen network into meshes.
2. Determine the number of uses as part of a mesh for each chain of the network.
3. Determine the maximum $u_{\max}(i)$, minimum $u_{\min}(i)$ and average $\overline{u}(i)$ number of uses for the chains of mesh i, $i = 1, \ldots, N$ using step 2.
4. Determine the type of entanglement of the two meshes i, j and determine its well-defined minimum number of crossings C_{ij}.
5. Evaluate

$$E_{\max} := \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{C_{ij}}{u_{\min}(i) \cdot u_{\min}(j)},$$

$$E_{\min} := \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{C_{ij}}{u_{\max}(i) \cdot u_{\max}(j)},$$

$$\overline{E} := \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{C_{ij}}{\overline{u}(i) \cdot \overline{u}(j)}.$$

The numerical values of $E_{\min}$, $E_{\max}$ and $\overline{E}$ denote minimum, estimated maximum and estimated average value for the number of physical cross-links of the chosen network. Note that $E_{\max}$ and $\overline{E}$ are estimated values, as will be discussed below, and the above definition is limited only to pairwise analysis using knot theory. Concerning analysis of more than two components this method can be extended accordingly.

5. Discussion

First we will show that $E_{\min}$ is a real lower bound for the number of physical links obtained by pairwise analysis of closed cycles. For this purpose let us consider the worst case where one entanglement is counted as often as possible. Consider two meshes, consisting of an arbitrary number of chains, each with an arbitrary number of uses. If the complete entanglement is concentrated on one single chain (or sequence of chains) at both meshes and that chain (or sequence of chains) at each case holds the highest number of uses, this would lead to a possible maximum number of detectable entanglement and to the largest possible deviance of reality; but this is exactly the definition of $E_{\min}$. Non-detectable entanglements cannot violate this minimum property.

Now we will discuss the validity of $\overline{E}$. We will start with a simple case and generalize the system stepwise to get an image of the complexity of the determination of trapped entanglements and additionally to see the arising problems. As starting point we choose the most simple special case of an infinite cubic lattice. Using the method of Franzblau each chain is four times part of a mesh. Let us consider an additional unknotted mesh only wrapped around one chain of the lattice once and not being part of the lattice. This additional mesh forms Hopf-links with all meshes of the network where the above chain is part of. Therefore this entanglement will be counted at each mesh at which that chain is found. Computation of $\overline{E}$ in this case would lead to an exact number of physical links.

As a next step of generalization let us consider again a cubic lattice with meshes obtained by Franzblau and one closed unknotted cycle placed additionally in that lattice not being part of the lattice. If we define the regular (no crossings are cut by the surface) minimum surface which is bounded by that cycle, we can count the edges of the lattice, which are cut by that surface. If their number equals one, we get the case discussed above. If their number equals two we can split up in two cases. I – First, the edges cut are part of one mesh: then there are two sub-cases: Ia – if the cycle is twisted one detects the Whitehead-link (or any similar link $6_3^2, 7_3^2, 8_6^2, \ldots$ depending on the number of twists) once and six times the Hopf-link, Ib – if not, one detects only six times the Hopf-link. II – Second, the edges cut are not part of one mesh. Then one detects eight times the Hopf-link independent of any twists. In case II our approximation methods yields the exact result. In case Ia we evaluate slightly more and in case Ib slightly less than the real number, if the whole structure would be known. Even for this simple case one cannot evaluate an expected value because the distribution of the twisted surfaces is not known and also the percentage of case II. Additionally there are again sub-cases of this simple case, which cannot be detected. See for example Fig. 9, where the entanglement in the middle cannot be detected.

One can consider more special cases leading to the result that the defined average value $\overline{E}$ reaches approximately the number of detectable physical cross-links. Regarding the non-detectable entanglements we assume that this average value is still a lower bound. Alike, it is impossible to verify the maximum property of $E_{\max}$, but we assume for random networks that this value is still an upper bound for the real value, because of the commonly big difference between $E_{\max}$ and $\overline{E}$. For the special systems of known chemical structure mentioned above $E_{\max}$ fails its maximum property.
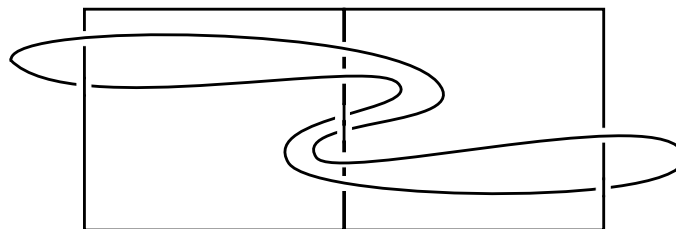

Fig. 9. The Entanglement in the middle cannot be detected by any analysis of meshes containing no common points.

One can test the accuracy of the approximation method also for the simple random-like examples of Figs. 4 and 6. Assuming equal chain length and using Franzblau one gets $E_{\max} = E_{\min} = \overline{E} = 1$ and $E_{\max} = E_{\min} = \overline{E} = 2$, respectively. The assumed equal chain length and the symmetry of the left part of each Figure leads to this exact result. Using our method and assuming equal probability for each decomposition into meshes one gets $E_{\min} = 2/3$, $E_{\max} = 4/3$, $\overline{E} = 8/9$ and $E_{\min} = 4/3$, $E_{\max} = 8/3$, $\overline{E} = 16/9$ which is closer to reality and therefore of more use than the uncorrected number of entanglements.

The difference between the maximum and the minimum number is caused by the diversification of the number of uses of the chains of one mesh. In order to get the best results possible we can formulate the criterion for the right selection of the algorithm for decomposition: the variance of the uses of the chains as part of a mesh should be minimal. In special cases, if the Franzblau-algorithm yields identical numbers of uses for every chain (diamond lattice, cubic lattice . . .), the values of $E_{\min}$, $E_{\max}$ and $\overline{E}$ are also identical and the Franzblau-method has to be chosen for the analysis. Random networks should be analyzed using our method, because of the lower numbers of usage and the higher resulting accuracy.

The importance of this procedure can be clarified, by considering the networks of Fig. 5. Their mean number of usage of about 3 results in a number of physical links about 9–15% of the number of entanglements detected. Therefore the number of detected entanglements cannot be used for a theoretical description of the networks without correction. Note that Fig. 3 of [22] was evaluated using the above method and the numbers in the tables of that paper are the uncorrected numbers of detected entanglements.

6. Some possible pieces of solution and a short outline of postulated properties of new methods

It is still unknown at which percentage the classical analysis of entanglements based on pairwise tests of closed cycles determines their real number. Due to this problem it is necessary to get additional or more general methods which are able to detect all kind of trapped entanglements. Not until the fraction of the "non-detectable" entanglements can be estimated conclusions concerning the elastic properties of polymer networks can be drawn. We will now discuss briefly some possible pieces of solution for some known problems to stimulate further developments.

One of the problems discussed above is founded on the basics of the mathematical theory used until now. The Alexander and the HOMFLY-Polynomial describe the topology of a number of closed cycles containing no common points. This is one problem in Fig. 9. One needs to check the three mapped meshes to be able to find the entanglement described, but for an analysis using one of the polynomials, this is not possible. But this problem can in part be solved using an idea of Vassiliev's first described in [47]. For a more convenient approach see [51] and for some general features of these invariants see [49,50,52]. It can be noted that Kauffman [30] also introduces a variant of the HOMFLY-Polynomials using this type of fixed crossings.

The basic innovation of this method is the generalization of the crossings analyzed. Chemical cross-links connecting four chains are introduced as fixed crossing of type L_x and an extended crossing-change formula is used for the removal of the crossings L_x. The crucial point of this crossing-change formula is that each step of removal doubles the number of links to analyze without decreasing the number of crossings. In 1993 an algorithm was verbalized and programmed by Deguchi and Tsurasaki [41] for knots and in 1997 by Stanford [48] to determine Vassiliev's invariants of knots and links. Applying this procedure one has also to be careful for an additional over-counting of the results analogous as above and one has to compare with the outcomes of the pairwise analysis of closed cycles. A valid analysis should combine both approaches and an extended version of our approximation method.

Unfortunately the use of Vassiliev's invariants is restricted to cross-links connecting four chains. Concerning random networks there is need for an other more general method or the analysis has to be restricted on suitable parts of the network. Nevertheless this new invariant seems to be the one step into the right

direction: note that the two cross-links connecting three chains in the Figs. 4, 6 and 9 can be contracted to one cross-link connecting four chains.

As pictured in Fig. 7 physical cross-links can be responsible for the formation of additional meshes, which cannot be detected by any decomposition when knowing just the chemical structure of the network. These additional meshes have to be included and the analysis has to be extended to more complex structure-entities than closed cycles. The greatest problem of this generalization is the increasing computing time caused by the exponential growth of the number of possible structure-entities by growing their size.

We can summarize this briefly: the basis for a solution of this problems is to select one mesh (or structure-entity), to cut all chains connecting this mesh (or structure-entity) with the part of the whole system spatially overlapped and to analyze the entanglement between both. This would lead to a determination of all possible Brunnian links or equivalent structures not detectable with hitherto methods and to a determination of the previous mapped examples. One has to think about possible over-counting of the same structure detected more than once.

7. Conclusion

In this article we discussed different methods to determine trapped entanglements of pairwise links regarding their advantages and drawbacks concerning computing time and accuracy. For increasing accuracy one has to change from the GLN to the Alexander-Polynomial or finally to the HOMFLY-Polynomial. If the computing time is the most important reason for a decision, the fast Alexander-Polynomial should be chosen.

Depending on the structure of the investigated network the algorithm for decomposition should be chosen. If there is no distribution in the length of the meshes the method of Franzblau should be taken. If the decomposition can be done in that way that the number of uses of every chain is the same that decomposition has to be taken. Otherwise our method is better suited. Independent of the set of meshes chosen one has to count the number of physical links using our approximation. The evaluated E_{min} is a real lower bound, the evaluated $\overline{E}$ is an approximative expected value and E_{max} is an approximative upper bound for random-like systems for the number of physical cross-links of detectable entanglements.

It was shown in several examples that until now in general no exact determination of physical cross-links is possible. Some basic problems of the existing methods are outlined briefly and Vassiliev's invariants are introduced as possible solution for a part of them. New methods must be found to get a more accurate determination of preferably all types of trapped entanglement for a further development of the theoretical description of polymer networks.

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