FIELD THEORIES AND THE PROBLEM OF TOPOLOGICAL ENTANGLEMENT IN POLYMER PHYSICS

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In this contribution some recent advances in understanding the statistical mechanics of topologically linked polymers will be reviewed. This is an interdisciplinary subject in which polymer physics, knot theory, and field theories meet together. Hopefully, we will convince more polymer physicists that field theories and knot theory are useful tools for their research and, on the other side, attract more theoretical physicists and mathematicians to polymer physics.

1 Foreword

Professor Hagen Kleinert is certainly one of the most brilliant contemporary scientists. One can hardly find a sector of theoretical physics in which he has not contributed with outstanding results. His books, constantly updated, are an invaluable source of information for many researchers. Coworking with him is a pleasure, even if sometimes it is not easy to cope with the amount of brilliant ideas and quick solutions of difficult problems which, miraculously, he is able to produce in a short time.

His achievements in polymer physics and in the theory of random walks are too many to be listed here (see for instance Refs. [1,2]). In my opinion, the most important of them has been the formulation of the problem of topological entanglement in terms of Chern-Simons (CS) field theories [2]. Here I will talk about a joint work on the statistical mechanics of topological polymers. This has led to the first quantitative physical prediction that could be extracted from a topological field theory.

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2 A Brief Introduction to the Physics of Polymers

2.1 Introduction to Polymers

In our everyday experience we are constantly in contact with synthetic polymers like plastics, rubbers etc., without mentioning the fundamental role for the existence of all living beings played by biopolymers like DNA, proteins, and viruses. The marvelous properties of polymer materials and their outstanding performances attract considerable interest from both chemists and physicists. A starting point to the vast realm of polymers from a physicist point of view is given in Ref. [3]. At a more specialized level, there are other excellent books (see Refs. [1,2,4]). A clear and concise explanation of advanced techniques of polymer physics can also be found in recent review articles, as for example Ref. [5].

Polymers are macromolecules composed of many units consisting of particular molecules called monomers. The latter are able to join together via covalent bonds forming very long chains. Artificial polymers may contain up to 16 000 monomers, while a biopolymer arrives to the astounding number of 10^{10} (ten billions!) monomers. The chains have macroscopic lengths which can be as long as a few meters in the case of biopolymers. On the contrary, in the remaining two dimensions their section is of the same size as the monomers, i.e. it amounts to a few Ångstroms. Thus, polymers may be treated as nearly one-dimensional objects.

Polymerized materials appear in a variety of forms with strikingly different features. For instance, plastics and rubbers are both solids, but certainly they do not have the same behavior under stretching. For this reason, in order to classify polymers, it is better to introduce the concept of phases instead of using the more traditional division in gas, liquid, and solid states. Four possible phases of polymers are distinguished [3]: viscous, elastic, semi-crystalline, and glassy phases. In the following, the viscous phase will be mainly discussed, which is liquid and contains the physically interesting cases of polymer melts and solutions.

2.2 Polymers and Physics

What opens the way to physics is the fact that, to a large extent, the differences in the macroscopical properties of polymer systems are not due to

the chemical composition of the monomers.[a] This is the so-called universal behavior of polymers. The main reason for such a universality is that polymers are almost macroscopical objects in one direction. At scales which are much larger than the monomer size, they can be considered for all practical purposes as very long and flexible tubes. Incidentally, this makes the study of polymer liquids easier than that of normal liquids, where the motion of a molecule depends on the motion of its nearest neighbors and on that of its next-to-nearest neighbors etc. Instead, the action of each monomer is "averaged" over all the chain length.

The flexibility of polymers is negligible at short distances, but after some monomer lengths it starts to show up. Thus, there should be a critical length a such that any segment shorter than a can be regarded as rigid. One usually calls a the length of the Kuhn segment, after its discoverer; it is a parameter which depends on the temperature. Typical experimental values of a are 1nm for the simplest synthetic chains and about 100 nm for DNA. It can also be shown that the memory of the orientation of a given monomer gets completely lost after a distance greater than $a/2$. As a consequence, it is possible to describe a vast class of polymers using a model of freely joint segments of equal length a. In this picture polymers are treated as random chains subjected to thermal fluctuations. Of course, there are a few different mechanisms of flexibility, which make some macromolecules more rigid than others. Some methods to take into account the rigidity of the joints are reported in Refs. [2,6].

Still an important question has been left unanswered. What is driving the behavior of polymers at large scales if not their chemical compositions? The answer is: the entropy of the system. In fact, the computation of the entropy and of the free energy is the fundamental problem of the statistical mechanics of macromolecules. To understand how entropy is relevant for describing polymer systems, it is sufficient to consider the example of a single chain. The trajectory of an unstretched chain is able to entangle in an infinite number of different configurations like the path of a particle subjected to random walk. When it starts to get stretched, however, the entanglement freedom decreases, so that this simple system moves from a more probable state (realized in more different ways) to a less probable one (realized in fewer

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[a]Of course, this claim should not be taken in a too strict sense. For instance polyelectrolytes, i.e. polymers in which the monomers are charged, have a different behavior with respect to uncharged polymers.

ways). In the limit in which the chain is completely stretched, it becomes a straight line which has no freedom at all. Clearly, a stretched chain will attempt to return to the most probable state, reacting to the stress with an opposite elastic force. Indeed, the elasticity of polymer systems can be explained in terms of entropy alone.

2.3 Polymers and Field Theories

Let us assume that our system of polymers is at equilibrium and at constant temperature T. To compute the entropy and free energy, it is necessary to sum over all possible trajectories of polymers using numerical or path-integral techniques.[b] In either case, we apply the above large-scale picture of polymers as random chains. The chain length L, the number n of freely joint segments and the Kuhn length a are related together by $L = na$.

Let us remember at this point that we are talking about polymers in the liquid state. In the standard theory of fluids, it is better to deal with densities and currents instead of following the trajectory of each molecule. In the case of polymers it is also more convenient to work with monomer densities and currents. Besides, the density of monomers is easily controlled in the laboratory, while it is more difficult to measure the average polymer conformations in space. The passage from trajectories to monomer densities is analogous to the passage from first to second quantization in quantum mechanics. This procedure will be explained later.

One advantage of having a field theoretic model of polymer liquids is that it is possible to apply sophisticated techniques already developed in high energy and condensed matter physics to study critical phenomena [1]. In fact, even at constant temperature polymers have still a non-trivial critical behavior with respect to physical parameters like polymer length and monomer density. Field theories have played a crucial role in the achievement of a satisfactory microscopical model of the physics of linear (unentangled) open chains [7]. Some computations of the critical exponent of polymers with field theoretical methods are performed in Ref. [2].

Last but not least, we may expect the existence of something fundamental like a gauge principle behind the universality of the behavior of polymers. The first gauge field theory of polymers has been constructed in Ref. [8]. In the following we will see that topologically linked polymers are deeply related to

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[b]Path-integral techniques imply a continuous limit in which the finite monomer size is neglected because it is very small compared with the total length of the polymer.

topological gauge field theories.

3 The Problem of Topological Entanglement in Polymer Physics

3.1 Polymers and Knot Theory

As mentioned in the previous section, the present understanding of the statistical mechanics of linear open chains is relatively satisfactory. However, with increasing monomer densities, polymers find it convenient to entangle for entropy reasons. In principle, higher densities can be tackled in field theory using scaling arguments. However, in this way one may easily overlook the appearance of new effects like for instance the topological ones. In fact, both in natural and artificial substances there is an abundance of polymer rings, in chemistry also called catenanes, which often are linked together to form non-trivial topological configurations. In vivo, for example, the shape of DNA is usually that of a ring. On the other side, in industrial processes the formation of knots is controlled in order to obtain materials with desired viscoelasticity properties. Since trajectories of polymers are self-avoiding and cannot penetrate each other, once a system of polymers is created in a given topological state, this cannot be changed. Thus there are real topological constraints which remain stable in time. Again, entropy considerations explain the differences in the behavior of open and closed chains. These are due to the fact that the topological constraints reduce the possible configurations of the system.

3.2 Statistical Mechanics of Topologically Linked Polymers

Most attempts to derive a microscopical model of topological entanglement in polymer physics are based on the so-called Edwards' approach in which the polymers are considered as fluctuating random chains or rings and where the entropy is computed via path-integral techniques [9]. Moreover, one starts with open chains having fixed ends at the points $\mathbf{x}_1, \mathbf{x}'_1, \ldots, \mathbf{x}_N, \mathbf{x}'_N$, respectively. The case of closed polymers is recovered at the end in the limit of coinciding end points $\mathbf{x}_1 = \mathbf{x}'_1, \ldots, \mathbf{x}_N = \mathbf{x}'_N$.[c]

Since polymers are almost one-dimensional objects linked together, the language of knot theory is the most adequate to discuss their topological

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[c]The presence of fixed points is certainly a limitation because it is unphysical. Indeed, in the laboratory polymers fluctuate freely. However, this shortcoming may be eliminated by performing an average over all possible positions of the fixed points [10].

states. Accordingly, we define a link as a collection of N circles in $3-d$ space. Two links are said to be equivalent if they can be deformed one in another without breaking any line. It is possible to classify inequivalent links with the help of topological invariants. The latter are numbers remaining constant under any continuous transformation which maps a given link to an equivalent one. Clearly, topological invariants which explicitly depend on the trajectories of the polymers are needed to distinguish the topological configurations of a system of polymers. For physical purposes it is enough to have a finite set of sufficiently powerful topological invariants $\{\chi\} = \chi_1, \chi_2, \ldots$.

At this point we consider N linked polymers with trajectories $P_1, \ldots, P_N$ of lengths $L_1, \ldots, L_N$, respectively. The topological constraints are imposed by requiring that the topological invariants $\{\chi\}$ take given values $\{m\} = m_1, m_2, \ldots$: The fundamental problem of computing the entropy of the above system is solved once the following configurational probability is known:

$$G_m(x; L) = \sum_{\substack{\text{all paths } P_1, \ldots, P_N \\ \text{of lengths } L_1, \ldots, L_N \\ \text{and ends in } \mathbf{x}_1, \ldots, \mathbf{x}_N}} \prod_\sigma \delta(\chi_\sigma(P_1..P_N) - m_\sigma)e^{-\frac{V}{kT}}. \quad (1)$$

Here, k is the Boltzmann constant and V is the potential energy of the system, which will be specified later. The topological relations are fixed by Dirac δ–functions.

In principle, all mathematical tools to compute Eq. (1) can be borrowed from the theory of knots, but in practice the link invariants $\{\chi\}$ are given in the form of polynomials of one, two or three variables which have no evident connection to the physical conformations of the polymers. For this reason, the possibility of constructing knot invariants from Wilson loop amplitudes of field theories [11] has been welcomed with excitement. In fact, these amplitudes are correlation functions of gauge invariant and metric independent operators which explicitly contain the trajectories of closed curves in $3-d$. Alas, in mathematics it is sufficient to deal with static trajectories, but in the present context one has also to sum over all polymer conformations. To this purpose, the topological invariants obtained from field theories are too complicated to allow the evaluation of the configurational probability (1) in any closed form.

4 The Gaussian Approximation

4.1 The Gaussian Linking Number

Until now, the only topological invariant which has been successfully incorporated in the Edwards' approach is the Gaussian linking number (GLN) which is also called intersection number. For any couple of non-intersecting paths P_1 and P_2 it is defined as follows:

$$\chi(P_1, P_2) = \frac{1}{4\pi} \int_0^{L_1} ds_1 \int_0^{L_2} ds_2 \, \dot{\mathbf{x}}^1(s_1) \cdot \left[\dot{\mathbf{x}}^2(s_2) \times \frac{\mathbf{x}^1(s_1) - \mathbf{x}^2(s_2)}{|\mathbf{x}^1(s_1) - \mathbf{x}^2(s_2)|^3} \right]. \quad (2)$$

Here P_1 and P_2 have been parameterized in the standard way as curves in space. The significance of the GLN has been discussed for instance in Chap. 16 of Ref. [2].

The GLN has the advantage to depend explicitly on the polymer trajectories, but it is relatively weak in distinguishing different topological configurations. Strictly speaking, it can be used with high accuracy only when the monomer density is so low that the polymers cannot be linked together in a too complex way.

4.2 The Interactions Acting on the Monomers

Here we are rather lucky, because only the so-called repulsive steric interactions act on the monomers and thus contribute to the potential energy V of Eq. (1). These short range forces are responsible for the fact that the polymers cannot penetrate each other. When two monomers get too close, they experience an infinite potential barrier which causes the repulsion. Thus, the potential energy of the polymers can be written in terms of Dirac $\delta-$functions:[d]

$$V = \sum_{i,j=1}^{N} \frac{v_{ij}^0}{2a^2} \int_0^{L_i} ds_i \int_0^{L_j} ds_j \, \delta^{(3)}(\mathbf{x}^i(s_i) - \mathbf{x}^j(s_j)). \quad (3)$$

This completes the definition of the configurational probability given in Eq. (1). Are there really no other relevant interactions? The correct answer is yes, there are still the topological interactions necessary to maintain the system in a given topological state. To see how topological forces work

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[d] We suppose that the energy involved in the thermal fluctuations is so high that the monomers do not see the finest details of the two-body potentials.

on monomers, we rewrite the product of $\delta-$functions in Eq. (1) in the Fourier representation as follows:

$$\prod_\sigma \delta(\chi_\sigma(P_1..P_N) - m_\sigma) = \int \frac{d\lambda}{2\pi} \exp\left\{\sum_\sigma i\lambda_\sigma \left[m_\sigma - \chi_\sigma(P_1..P_N)\right]\right\}. \quad (4)$$

Physically, λ_σ denotes the chemical potential corresponding to the topological number m_σ. At this point we assume that the topological constraints are imposed in the Gaussian approximation i.e. by means of the GLN's $\chi(P_i, P_j)$, $i \neq j = 1, ..., N$. We see that now, in the exponent of Eq. (4), the $\chi(P_i, P_j)$ appear as two-body potentials given by Eq. (2).

4.3 A Path Integral Model of Polymers

For simplicity, only the case of two polymers will be treated here. The generalization to a system of N polymers can be found in Ref. [12]. We work in the Gaussian approximation so that there is only one topological number m corresponding to the GLN $\chi(P_1, P_2)$. Now it is possible to write explicitly the configurational probability of Eq. (1) in terms of path-integral sums over the trajectories P_1 and P_2:[e]

$$G_m(x; L) = \lim_{\substack{\mathbf{x}^1 \to \mathbf{x}'^1 \\ \mathbf{x}^2 \to \mathbf{x}'^2}} \int_{\mathbf{x}'^1}^{\mathbf{x}^1} \mathcal{D}\mathbf{x}^1(s_1) \int_{\mathbf{x}'^2}^{\mathbf{x}^2} \mathcal{D}\mathbf{x}^2(s_2) e^{-(\mathcal{A}_0 + V)} \delta\left(\chi(P_1, P_2) - m\right), (5)$$

where $\mathcal{A}_0$ is given by:

$$\mathcal{A}_0 = \frac{3}{2a} \sum_{i=1}^{2} \int_0^{L_i} \dot{\mathbf{x}}^{i\,2} \, ds_i. \quad (6)$$

We notice that, following Edwards' approach, the configurational probability has been defined here starting from a system of open polymers[f] and then taking the limit of coincident extrema (see Section 3.2).

4.4 From Polymers to Fields

First of all, one observes that the trajectory of a randomly fluctuating chain and the trajectory of a particle subjected to a Brownian motion have many

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[e]Hereafter, the temperature will be incorporated in other constant numerical factors and will thus be ignored.

[f]In this case $\chi(P_1, P_2)$ is no longer a topological invariant.

similarities. Indeed, the action of Eq. (6) describes the free random walk of two particles. This duality between polymers and particles is explained in details in Ref. [1]. In this way, the statistical problem of polymers becomes equivalent to that of particles subjected to self-avoiding random walks which are constrained to satisfy given topological relations. At this point, the desired final mapping to field theories could be performed in principle exploiting the wave-particle duality present in statistical mechanics as in quantum mechanics. However, a first technical difficulty arises: In this "second quantization" procedure one encounters expressions of the kind $\log Z$ or Z^{-1}, where Z is the partition function of a Landau-Ginzburg field theory interacting with topological fields. Such nonlinear terms can be simplified exploiting the well known limits (method of replicas): $\log Z = \lim_{n \to 0}(Z^n - 1)/n$ and $1/Z = \lim_{n \to 0} Z^{n-1}$.

The presence of a Dirac $\delta-$function in the configuration probability of Eq. (5) is not a terrible obstacle, since it may always be put in the more convenient form of Eq. (4) after a Fourier transformation. However, after doing that, one finds that the resulting particle action (i.e. the former polymer action) is non-Markovian. Moreover, even in the Gaussian approximation the topological interactions give rise to a potential which couples the trajectories in a nonlinear and complicated way (see Eq. (2)). For this reason, the "second quantization" of such a system has been a difficult long-standing problem for more than twenty years, which could be solved only recently with the help of CS field theories [13].

5 A Field Theoretical Model of Polymers

Skipping all details, which can be found in Refs. [12,13], the above "second quantization" procedure arrives at a model of linked polymers which consists of N Landau-Ginzburg field theories of the kind

$$\mathcal{A}_{\mathrm{L-G}} = \sum_{i=1}^{N} \int d^3x \left[|\boldsymbol{\nabla}\psi_i|^2 + m_i^2 |\psi_i|^2 \right], \tag{7}$$

with $i = 1, \ldots, N$, which are minimally coupled to Abelian CS fields.[g] The latter "propagate" the long-range topological interactions. In the language of

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[g]Actually, things are a little bit more complicated than that: According to the method of replicas, anyone of the above N systems must be replicated a number n_i of times. The physical configurational probability is then obtained in the limit of zero replicas.

fields, the monomer density of the $i-$th polymer is $|\psi_i|^2$, while the masses m_i are Boltzmann factors controlling the polymer lengths. The polymer lengths approach infinity in the limit of zero masses. If also the repulsive steric interactions are considered, one should add suitable quartic interaction terms for the complex fields ψ_i, ψ_i^*.

6 Applications and Conclusions

Field theories provide an exact description of a system of N fluctuating polymers in terms of a topological Landau-Ginzburg model. Previous difficulties of the Edwards' approach have been solved by decoupling the nonlinear interactions between the trajectories due to the topological potential (2) with the help of Abelian CS fields. CS field theories are topological and enjoy many special properties. For instance, they are supposed to have only finite radiative corrections and their Hamiltonian is zero in the absence of couplings with matter fields. As a consequence, it is licit to suppose that the topological interactions do not change the critical properties of polymers. Indeed, this has been explicitly checked in a semi-classical approximation, valid in case the monomer density is sufficiently high to be considered as uniform [14]. In the same approximation, it has been shown that topological forces are attractive in agreement with experimental observations.

Moreover, the square average GLN $\langle m^2 \rangle$ of two fluctuating polymers may be exactly computed by field theoretical methods [10]. With some approximations, this result has been applied to estimate the average square number of intersections $\langle m^2 \rangle$ formed in a solution by a test polymer P of length L with the other polymers [10]:

$$\langle m^2 \rangle \sim \frac{a^2 \rho L}{18 m_a \pi^{\frac{1}{2}}}.$$ (8)

Here ρ represents the average mass density of the polymers per unit volume and m_a is the mass of a single segment. Eq. (8), which is valid in the limit $L \gg 1$, provides an approximate formula for the probability of knot formation inside polymer solutions. The relation (8) has been obtained after averaging over all possible fixed points (see Section 3.2). Curiously, if a segment of P is anchored at a given location $\mathbf{x}$, $\langle m^2 \rangle$ does no longer depend on L! This difference can be explained by the fact that topological interactions are attractive. Since knotted polymers get closer than unknotted ones, the chance increases that they become more and more topologically entangled. On the

contrary, if their trajectories are fixed at some points, the attractive forces become irrelevant.

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