Topological Polymers: An Application of Chern-Simons Field Theories

Franco Ferrari[1], Hagen Kleinert[2], Ignazio Lazzizzera[3]*

[1] Institute of Physics, University of Szczecin, ul. Wielkopolska 15, PL-70-451 Szczecin, Poland
[2] Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany
[3] Dipartimento di Fisica, Università di Trento and INFN, Gruppo Collegato di Trento, via Sommarive 14, I-38050 Trento, Italy

Summary: After a brief introduction to the statistical mechanics of polymers, it will be shown how abelian topological field theories of the Chern-Simons type enter naturally in the description of a system of linked polymers, solving the difficulties of previous approaches. A field theoretical model of topological polymers will be presented and some of its physical predictions on the statistical behavior of polymers in a solution will be discussed.

Introduction

In more than fifty years of developments, quantum field theoretical methods have become a powerful and reliable tool to study physical phenomena, as it is shown for instance by their success in condensed matter and high energy physics. Calculations are usually based on perturbation expansions organized by Feynman diagrams, which are direct pictures of the world lines of the particles in space-time. If the metric of space-time is taken to be euclidean, the world lines correspond to grand-canonical ensembles of fluctuating lines. For this reason, euclidean quantum field theory becomes a powerful tool for describing many physical systems whose properties are dominated by line-like excitations. Examples are vortex lines in superfluid helium and superconductors whose proliferation leads to the superfluid and superconducting phase transitions, dislocation and disclination lines in crystals where they explain the process of crystal melting.[1]

The application to line-like systems was pioneered in the seminal work of Edwards and de Gennes.[2,3] Thanks to their results and successive developments, our knowledge of the statistical properties of linear polymer chains and of polymer rings entangled with various obstacles has reached a somewhat satisfactory stage. It is impossible to review, in this short article, all important contributions to polymer physics based on the field theoretic description, and it would be superfluous since concise and exhaustive reviews

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of the subject are available in the literature.[4-7] Here we will limit ourselves to discuss the statistical mechanics of interlocked polymer rings (IPR's), also called *catenanes* in the chemical literature.[8] The construction of a self-consistent model of IPR's in solution at semi-dilute monomer concentrations beyond mean-field approximation was a long-standing problem, which has been solved only recently. The details of the construction of this model can be found in.[9-11] In this report we shall briefly describe it and emphasize its physical properties and predictions.[11-13]

Statistical Approach to IPR's

Before we come to the technical details, let us first explain what our model is supposed to describe and what is its range of applications. Polymers are complicated macromolecules and so far it has been impossible to set up a single model for the behavior of all polymer materials which can be produced nowadays. Here we consider the statistical mechanics of long and flexible polymers in a liquid state, which may be polymer solutions and melts. Polymers can exist in closed and open configurations, and their coexistence will be taken into account, but cross-link formation will be neglected, which would give raise to branched polymers. Moreover, we suppose that there are no charged monomer units in the liquid, thus eliminating polyelectrolytes. Since we are looking only for macroscopic properties, polymers will be treated as random chains with finite step size a. Although the random-chain approximation neglects the rigidity at the polymer joints, it is capable of capturing the large-scale features of a vaste class of polymers by a suitably choice of the parameter a, for example, $a=1nm$ for polyethylene, or $a=100nm$ for a strand of DNA. Due to the fact that we are dealing with very long polymers, the size of a is always small in comparison with the total length of the polymers. Thus, each polymer may be viewed as a continuous curve in the space.

The system is furthermore assumed to be in thermodynamic equilibrium and at a constant temperature T, described as a canonical ensemble. The fundamental problem to be solved is the computation of the partition function Z, which can be written as a sum over the set of allowed polymer conformations weighted by the Boltzmann factor $\exp(-H/kT)$:

$$Z = \sum_{conformations} \exp(-H/kT) \qquad (1)$$

where H denotes the potential energy of the system, while k is the Boltzmann constant.

The potential energy in H contains all atomic and molecular forces acting on the monomers. In principle, the forces are very complicated and should be treated with the methods of quantum mechanics. However, since we are observing polymers at a mesoscopic scale of distances, quantum interactions are averaged over several monomer lengths and this leads to drastic simplifications. Experimentally, only the so-called excluded volume interactions seem to be relevant as long as athermal systems are only regarded. These are short-range and highly repulsive forces, which repel two polymer segments when they are getting too close to each other. In a good approximation, they may be described by a phenomenological two-body potential in which the repulsion between two monomers is expressed in terms of a Dirac delta function.[2-6]

An important property of polymer liquids is that they contain also a sizable percentage of IPR's, which are linked together in a topologically non-trivial way. This has a deep influence on the characteristics of polymerized materials. For instance, there are changes in the elasticity properties of rubbers. In biology, topological constraints pose obstacles to vital processes in living cells, like DNA recombination and replication. The macroscopic effects caused by topological constraints are of entropic origin: they occur due to the fact that the topological entanglement of the trajectories limits the set of allowed configurations of the system.

To specify the topological state of the IPR's, to be denoted by Ω, consider the simplest kind of topological constraints. Suppose that there are N polymers with trajectories $P_1,\ldots,P_N$ inside the liquid. We require that for each couple of trajectories P_i and P_j $(i,j=1,\ldots,N)$, P_i winds around P_j a given number m_{ij} of times. The advantage of these conditions is that the winding number between the two paths P_i and P_j can be explicitly written as follows:

$$\chi(P_i,\, P_j) \;=\; \int_{P_i} d\vec{x}_i \int_{P_j} d\vec{x}_j \left[\times \; \frac{(\vec{x}_i \,-\, \vec{x}_j)}{\left|\vec{x}_i \,-\, \vec{x}_j\right|^3} \right] \tag{2}$$

Where $\int_P$ denotes the line integral along the path P. Note that the winding number has the form of a two-body potential of the Biot-Savart type. Indeed, it is possible to give a magnetic meaning to it.[14]

The interpretation of $\chi(P_i,P_j)$ as a potential has a physical motivation which goes beyond the topological origin. Topological interactions act on the monomers to keep the system of closed polymers in the given topological state Ω. But the integral for $\chi(P_i,P_j)$ has a certain value also if the trajectories P_i, P_j are not closed, although it loses its topological significance of being the winding number. In this case $\chi(P_i,P_j)$ can be considered as a phenomenological potential which influences the entanglement of open polymer chains.

It is remarkable that the winding number is the only link invariant with the form of a two-body potential that can be constructed from a local gauge field theory of the Chern-Simons type using the methods pioneered by Witten.[15] There exist more sophisticated link invariants, but these are all related to higher-order interactions, which take into account the collisions of three or more monomers at once. These interactions are negligible unless the monomer density in the liquid is really high, which we shall exclude here.

The Model

To keep notations as simple as possible, we suppose here that there are just two polymers in our system, so that the topological constraints over their trajectories are given by the condition $\chi(P_1,P_2)=m$. The number m is allowed to take only integer values if both polymers are closed. In this case, the above condition may be implemented inserting into the partition function Z the Kronecker delta:

$$\delta_{\chi(P_1,\, P_2)} \equiv \int_0^{2\pi} \frac{d\lambda}{2\pi} \exp - i\lambda\left(m - \chi(P_1, P_2)\right) \qquad (3)$$

If one polymer has an open trajectory, one should impose the constraint using a continuous Dirac delta-functions. The statistical mechanics of the above two-polymer system may be translated into that of a magnetic system with vanishing internal degrees of freedom.[9,12] Roughly speaking, in this passage one loses the notion of polymer trajectories altogether and deals instead with monomer densities and currents. This is analogous to the case of normal liquids where it is often preferable to work with molecular densities and currents rather than following the orbital paths of all molecules.

As we discussed in the previous Section, topological interactions have analogies with magnetic interactions. In the present context, the charge is associated to the orientation of polymer trajectories. For instance, one could assign a positive charge to a monomer located on a trajectory with a given orientation and a negative charge to a monomer located on the same trajectory, but with opposite orientation. As a consequence, the description of a system of two polymers requires charged fields ψ_1, ψ^*_1 and ψ_2, ψ^*_2,, $i=1,2$. The monomer density and current of each polymer are given by $\rho_i=|\psi_1|^2$ and $\Im[\psi^*_1 \nabla\psi_1]$, respectively, where $\Im$ denotes imaginary part. In praxis it is convenient to use multiplets of replica fields Ψ_i,Ψ^*_i, but due to the lack of space it will not be possible to review the method of replica here.

To propagate the topological interactions corresponding to the potential $\chi(P_1,P_2)$ we need a theory which is similar to electromagnetism, but does not introduce any extra energy in the system. Note our previous remark that topological constraints influence only the entropy of the system, not the internal energy. These characteristics are fulfilled by describing the topological interaction with the help of two vector fields which are coupled to the polymers like a magnetic vector potential to a line-like current and whose action is of the Chern-Simons type:

$$A_{CS} = ik \int d^3x \vec{a}^{(1)} \cdot \left(\nabla \times \vec{a}^{(2)}\right) \tag{4}$$

Omitting all details of the derivation, the total action of the two-polymer model is given by:

$$A_{pol} = A_{CS} + \sum_{j=1}^{2} \int d^3x \left[\left| \left(\nabla + i\gamma_j \vec{a}^{(j)}\right)\Psi_j \right|^2 + \mu_j^2 \left|\Psi_j\right|^2 \right] + \alpha \sum_{j,l=1}^{2} d^3x \left|\Psi_j\right|^2 v_{jl}^0 \left|\Psi_l\right|^2 \tag{5}$$

The coupling constants γ_1 and γ_2 depend linearly on the Chern-Simons coupling constant

k and on the *topological* parameter λ respectively. The parameter μ_i is the Laplace conjugate variable of the polymer length L_i. In the limit $\mu_i = 0$, polymers are allowed to be infinitely long. Finally, α is proportional to a^{-4}.

Results and Conclusions

The microscopical model briefly described here leads to a self-consistent description of polymers in solutions at semi-dilute monomer concentrations. At such concentrations it is sufficient to take into account only the collision probability of pairs of monomers, disregarding higher-order interactions. An advantage of having a field theoretic formulation is that in this way it is possible to apply powerful techniques already developed in high-energy and condensed-matter physics, such as for instance renormalization group theory.[16] Moreover, with the help of field theoretical methods it is possible to investigate the properties of very long polymers forming complicated topological states, a situation which becomes challenging for numerical simulations since it requires a big amount of computer resources.[17] In principle, one could define a formal partition function in which polymers are subjected to much more sophisticated topological conditions than those used in this work. However, without a mapping into a field theory, it would be hard to extract from such partition function any information about the statistical behavior of the polymers by means of analytical calculations.

Let us conclude by listing some consequences of our model:

1) The model looks similar to a Ginzburg-Landau field theory of superconductors, with a quartic interaction term which takes into account the excluded volume forces, coupled to Chern-Simons fields. The latter propagate the forces of entropic origin which keep the system in the given topological state.
2) The critical behavior of polymer rings subjected to excluded volume interactions is not changed by the presence of topological constraints. This statement is based on the common belief that the coupling of Chern-Simons field theories to another field theory cannot modify the renormalization group equations of the latter. An explicit check has been done however only in the semi-classical approximation.[11]
3) Using the method of the effective potential, it has been possible to show that one effect of the topological interactions is to screen the repulsive excluded volume forces. As a consequence, IPR's tend to get closer to each other than unknotted polymer rings. This effect has been effectively observed in the case of the DNA of bacteria.[18]
4) There are many analogies between IPR's and topological defects. Multi-component Chern-Simons field theories like that used here to describe the statistical mechanics of IPR's, have been studied in connection with topological defects and spontaneously broken symmetries in.[19] The results of [19] suggest that also the physics of IPR's may still yield unexpected and exotic phenomena of a non-perturbative nature.
5) The scaling behavior of the total average square winding number $<m^2>$ of a polymer

inside a solution has been calculated in.[12,13] The result at the first few orders in the polymer length L of the polymer is:

$$\left\langle m^2 \right\rangle \approx AL + BL^{\frac{1}{2}} \tag{6}$$

where the exact values of the constants A and B have been computed in [12,13] in terms of the monomer density and other physical parameters. The above formula allows to estimate the rate of link formations of a polymer in solution with other polymers.

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