

Stuart G. Whittington De Witt Sumners
Timothy Lodge
Editors

Topology and Geometry in Polymer Science



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With 67 Illustrations



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FOREWORD

This IMA Volume in Mathematics and its Applications

TOPOLOGY AND GEOMETRY IN POLYMER SCIENCE

is based on the proceedings of a very successful one-week workshop with the same title. This workshop was an integral part of the 1995–1996 IMA program on “Mathematical Methods in Materials Science.” We would like to thank Stuart G. Whittington, De Witt Sumners, and Timothy Lodge for their excellent work as organizers of the meeting and for editing the proceedings.

We also take this opportunity to thank the National Science Foundation (NSF), the Army Research Office (ARO) and the Office of Naval Research (ONR), whose financial support made the workshop possible.

Avner Friedman

Robert Gulliver

PREFACE

This book is the product of a workshop on Topology and Geometry of Polymers, held at the IMA in June 1996. The workshop brought together topologists, combinatorialists, theoretical physicists and polymer scientists, who share an interest in characterizing and predicting the microscopic entanglement properties of polymers, and their effect on macroscopic physical properties.

Linear polymer molecules in dilute solution are highly flexible and self-entangled. In more concentrated solutions, or in the melt, there can be important entanglement effects both within and between polymers, and these entanglements can influence the rheological properties of the system as well as the crystallization properties, and hence the properties of the polymeric system in more ordered states. Although polymer scientists have been aware of these problems for more than forty years, it is only recently that the powerful methods of algebraic topology have been used systematically to characterize and describe these entanglements. Starting from the simplest possible system (a ring polymer in dilute solution) one can ask how badly knotted the polymer will be, as a function of the degree of polymerization, the stiffness, the solvent quality, etc. To some extent these questions have been answered by a combination of rigorous mathematical arguments (combining ideas from combinatorics and from algebraic topology) and numerical methods such as Monte Carlo techniques. For instance, the paper in this book by Orlandini *et al* addresses the question of the relative probability of different knot types in a ring polymer. One can also ask about the differential geometry of the polymer and the paper by Bickis investigates this question for a random walk model. As the concentration increases, linking between rings becomes possible and these links will influence the static and dynamic properties of the solution. Several problems associated with linking are treated in this book by Diao and Janse van Rensburg and by Uberti *et al*.

As we pass from dilute solutions to melts the characterization of the entanglements becomes more difficult. The paper by Edwards addresses these problems. Having characterized the entanglement complexity one then needs to know how it will affect rheological properties. For instance, what is the contribution of entanglements to the elastic properties of a rubbery polymer? How do the dynamics of polymers, in solution or in the melt, depend on entanglement?

The conformations of polymers are strongly influenced by any applied geometrical constraints. Polymers behave quite differently in pores or when confined in a slab geometry and their properties in these environments influence their behaviour as, for instance, stabilizers of colloidal dispersions. Approximate theories of colloidal stability have been available for many years, but it is only recently that simple models of polymers in confined geometries have been analysed rigorously. There can be interesting inter-

actions between topological properties and these geometrical constraints. E.g. how does the knot probability in a ring polymer change when the polymer is confined to a pore or slab? These questions are treated in the papers by Soteros and by Tesi *et al.*

Topological problems also occur in the modelling of polymeric membranes. These are closely related to self-avoiding random surfaces, an area in which rapid progress has recently been made, although many important questions still remain open. Closely related are the properties of vesicles where the topology of the surface can have an important influence on the behaviour of the vesicle. The papers by Einstein and Stella, and by Beichl and Sullivan, discuss numerical approaches to these problems, while Janse van Rensburg presents some corresponding rigorous results.

An area where ideas from physics have had a direct influence on knot theory is the topic of *knot energies*. A knot is a simple closed curve in R^3 (which could be a smooth curve or a finite polygon). One associates an energy functional with the curve so that each embedding has an associated energy. The minimum energy over all embeddings with a fixed knot type is a knot invariant. The book contains four articles on this subject. The paper by Kauffman *et al* describes one such functional and the search for its energy minima. Of course, there is tremendous flexibility about the choice of the energy functional and the paper by Ernst *et al* considers desirable properties of the knot energy and compares different choices for it. The papers by Simon, and by Kusner and Sullivan discuss aspects of a closely related issue, the thickness of knots. This is an area which is attracting considerable interest at the present time, with recently observed correspondences between the electrophoretic mobility of knotted DNA circles and the energy of "ideal" knot representatives.

The book gives an account of recent progress in our understanding of polymer geometry and topology, and the physical ramifications of polymer entanglement. We trust that it will be of interest to specialists in this area. We hope that it will also serve to introduce polymer scientists to topological approaches, and topologists to interesting applications of their subject in polymer science.

Stuart G. Whittington

De Witt Sumners

Timothy Lodge

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ENTANGLEMENTS OF POLYMERS

S.F. EDWARDS*

Abstract. The interaction of polymers must not allow them to pass through each other. This poses a topological problem which strictly speaking is not solved. Nevertheless much progress can be made using the Gaussian invariant, and the way to do this is reviewed below. It turns out to give a renormalisable quantum field theory, and is effective in understanding experimental results.

1. The mathematics of polymers. Polymer molecules are totally understood in their specification, but their long chain nature introduces highly complex dynamics, for the chains not only have the dynamics of connection but also cannot pass through one another. Much progress has been made on dense systems, but the topological integrity of the molecules is ignored in dilute solutions, both in self or mutual interactions for no better reason than it is difficult to handle.

Suppose we study the configuration of a chain of N segments of length l , freely hinged, and of no thickness with no interactions. This problem is well known and of course completely soluble. For N large i.e. $N^2 \gg N$ the distribution of one end with the other end at the origin tends to

$$(1.1) \quad \left(\frac{3}{2\pi Nl^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3R^2}{2Nl^2}\right)$$

which is the solution of

$$(1.2) \quad \left(\frac{\partial}{\partial s} - \frac{1}{6}\nabla^2\right)P(R, s) = \delta(R)\delta(s)$$

were $s = Nl$.

To get P , this Fick equation is fine, but it cannot solve the problem of a polymer threading its way through a hole in a plane barrier, for the condition that at some s the polymer is at the hole, and at all other points of the plane the probability of tending the polymer is zero (for it cannot cross the plane except at the hole), and these two conditions are incompatible when using (1.2).

A real polymer of freely hinged segments is difficult to handle mathematically for its mathematical structure is of a continuous function of its arc length $R(s)$, which is not differentiable at $s = ml$, m integral, where the tangent R' changes direction abruptly. A model much studied is to allow the locus $R(s)$ to be differentiable, but have its second derivative R'' to change abruptly.

In terms of Wiener integrals, the Fick equation model is to use a prob-

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ability for the whole chain of

$$\omega \exp\left(-\frac{3}{2l\delta/2} \int R'^2(s)ds\right)$$

and for the 'worm like chain

$$\omega \exp\left(-\frac{3}{2l\delta/2} \int R''^2 ds\right) \prod \delta(R'^2 - 1)$$

or more crudely

$$\omega \exp\left(-\kappa \int R''^2 ds - \gamma \int R'^2 ds\right)$$

where k represents the energy of bending over kT and γ fits the long range size Nl^2 . Such molecules do exist and are important e.g. DNA, but as a model it obviously is a crude representation of say polystyrene.

These matters are dealt with in detail in textbooks^(1,2,3) and I assume the reader knows this or will study the books cited.

In order to give the reader an intuitive view of what worries polymer theorists, I pose the problem which will be calculated in section.

Imagine a box full of long random flight loci which are all frozen except one. Hold the ends of that fixed, but otherwise allow it to move in Brownian motion. The surrounding loci will hold our free locus in what is roughly a tube. What is the radius, a of this tube. It can only depend on c the concentration of the other loci, and l , but is not determined by dimensional analysis

$$a = a\left(\frac{L}{V}, 1\right) = a(c, l)$$

L total length of all the loci, V volume of the box:

$$a = l(cl^2)^\alpha$$

What is α ?

2. Topology and polymers. For an unambiguous situation consider two perfect circular rings, $R_1(s), R_2(s)$. They are either joined, or free. The criterion given by Gauss is that

$$(2.1) \quad I = \oint dR_1 \times dR_2 \cdot \nabla |R_1 - R_2|^{-1}$$

is zero for free rings, non zero for non free rings. The sign of I depends on the convention assigned to the direction of the tangent. This is already a problem as the molecule does not have a sense for its tangent, and this turns out to be tiresome in applications; but this paper will not get that far.

When one considers more than two rings e.g. the three Borromean rings one finds it easy to get a configuration such that $I_{12} = I_{23} = I_{31} = 0$, but the rings are entangled. Also there is no analogue of the Gaussian integral (2.1) for self knots e.g. the simplest trefoil knot. By projecting the locus of the curves in space onto a surface, and labelling each intersection on that surface according to which curve is nearest to the surface, one can construct Alexander polynomials, and new Vaughan Jones polynomials have recently appeared. These do not seem to be suitable for use in statistical physics however, though there are papers using them in simulations. The power of the gauss integral can be expressed this way:

Suppose we have a box of rings. The $I_{ij} = 0$ for all pairs. Thus the entropy of the system is

$$(2.2) \quad S = k_B \log \int \exp \left(-\frac{3}{2l} \sum_i \int R_i'^2 ds_i \right) \prod_{\alpha\beta} \delta(I_{\alpha\beta}) \prod_i DR_i.$$

This is complete and explicit. One could feed the $R_i(s)$ into a computer and evaluate. More to the point, one has an explicit formula to start from and calculate. Of course this is a peculiar system and would permit higher connections such as the Borromean rings, but one can imagine a system which really is represented by (2.2).

One can make rings, but very long polymers will have their topology dominated by local effects. It seems reasonable, particularly if a system is cross linked chemically thus freezing in its topology, that there is a good problem to be studied via (2.2) i.e.

Fig (1) cannot turn into figure (2). The shaded regions represent the rest of the system. This situation is covered by making I_{12} a constant.

To do this requires two further steps. The first is to be able to evaluate the integrals, the second is to recognize that the statement 'make I_{12} a constant' implies what in statistical mechanics is called a quenched system i.e. one must calculate the entropy for a given set of I_{ij} then average that entropy (the logarithm as in 2.2) over the initial and henceforward permanent values of the I_{ij} . This latter step is discussed in many papers and a particular method, the replica method, has been invented to handle it. It will take us too far away from topology to discuss this, so a simplified version will be offered later.

3. The evaluation of Gaussian invariants. Fick's equation (2.1) is like the Schrodinger equation and albeit "non relativistic" the evaluation of integrals of the Gauss type is like a field theory calculation. Such calculations started in the thirties but ran into divergence problems but in the forties it was realised that the divergence in some of the field theories was not an insuperable barrier to calculations for experiments measured the difference between the value of the field theoretic integrals when say

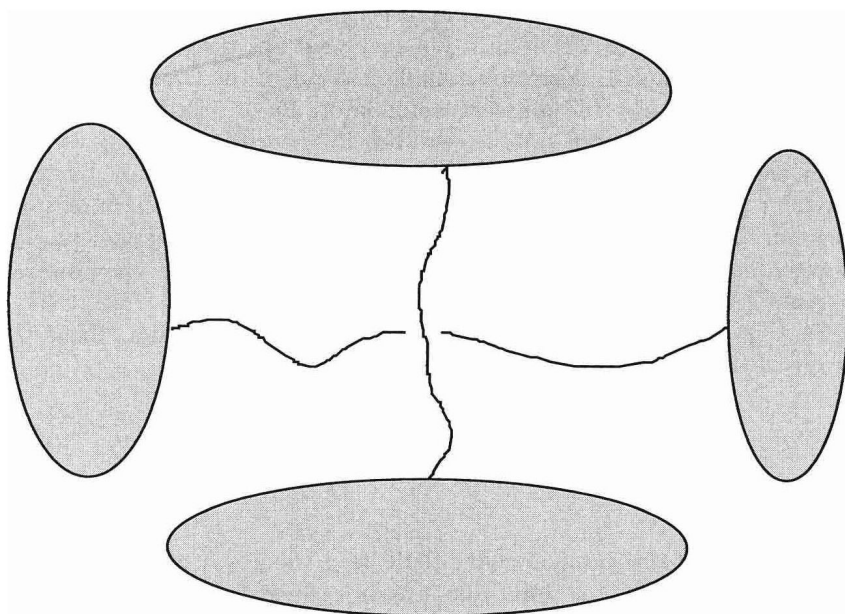


FIG. 1.

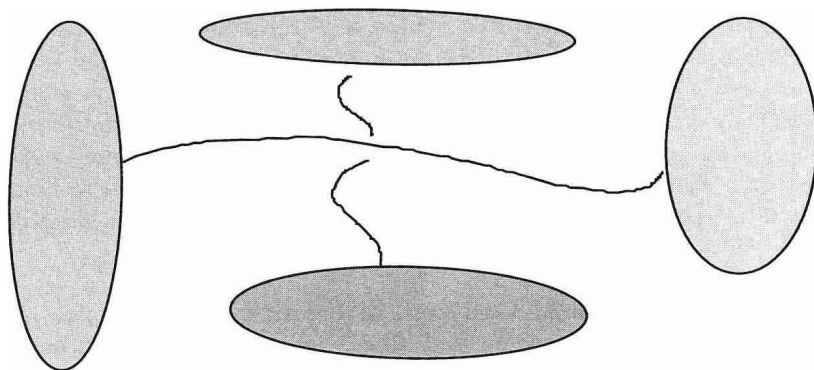


FIG. 2.

an external field is present. A typical integral might be

$$(3.1) \quad J(A) = \int_1^\infty \frac{dx}{x+A}$$

where experiment measures

$$(3.2) \quad J(A) - J(0) = \int_1^\infty \frac{dx}{x+A} - \int_1^\infty \frac{dx}{x}$$

$$(3.3) \quad = -\log(1+A).$$

This process, called renormalisation, is now fifty years old and so hallowed by time. Nevertheless, at a fundamental level one is faced by the fact that as A becomes large the integral becomes large, and if our present theories are inadequate at short distances and times, this inadequacy will show up at large A , i.e. at large external fields.

In polymers everything must be finite; the question we are addressing is whether one can discard finiteness guarantees and use Wiener type integrals to simplify calculations.

The first point is that the Gaussian invariant is the manifestation of a divergent but renormalisable field theory. The present author was able to prove this long ago⁽⁴⁾ by showing that the Gaussian integral could be parametrised by a vector field $A_i(v)$ via a Lagrangian

$$(3.4) \quad \sum \int R^2 ds + \mu \int A \cdot R' ds + \lambda (A_k \times A_{-k}) \cdot k d^3 k$$

(Similar things have been done in high energy field theories recently by Chern and by Simons.) Since this point will appear soon further detail will not be given here; the argument below is self contained.

As a caution it should be remarked that it is possible to get wrong answers by renormalisation, for example if one calculates the osmotic pressure of a polymer solution the answer is

$$(3.5) \quad wc^2 + \int \log \left(1 + \frac{wc}{k^2} \right) d^3 k$$

where w is the interaction and c the concentration. This is renormalised by removing a self interaction term $wc \int \frac{d^3 k}{k^2}$ to leave a finite term⁽¹⁾

$$(3.6) \quad wc^2 - b(wc)^{\frac{3}{2}}$$

If c becomes small, the fluctuation $c^{3/2}$ exceeds the mean c^2 and a negative osmotic pressure results which is physically impossible. If all the correct physical limitations to the theory are added, the theory becomes sensible. Crudely speaking, one just cuts off k at l^{-1} above and $(Nl)^{-1}$ from below. (In quantum field theories, relativistic invariance prohibits such cut offs.)

4. Calculation of the tube^(6,7,8). Firstly consider a crude argument. Suppose our polymers are swollen to a cylindrical shape of cross section πa^2 and then completely fill space⁽⁵⁾

$$(4.1) \quad \begin{aligned} \text{Then} \quad \pi a^2 L &= V \\ a &= (c\pi)^{-\frac{1}{2}}. \end{aligned}$$

But suppose that we argue (1) that calculations using Wiener measure can only give answers depending on $(Ll)^{\frac{1}{2}}$. Then

$$(4.2) \quad \begin{aligned} a &= c^\alpha l^{2\alpha+1} \\ &= V^{-\alpha} L^\alpha l^{2\alpha+1} \end{aligned}$$

hence

$$(4.3) \quad \begin{aligned} 2\alpha + 1 &= \alpha \\ a &= c^{-1} l^{-1} \end{aligned}$$

(Experimentally (9)a is available and lies between 1 and 1/2). These two results can be derived from the Gaussian integral where (4.1) results from differentiable chains and (4.3) from strictly Wiener chains i.e. continuous but not differentiable.

I will not go into the detail of the calculation here, but just outline it. One assumes there is an 'a' and evaluates it by considering the model of section (1) above i.e. one chain has fixed ends and moves amongst all the others which are frozen. Then consider our special chain at two remote times $R_1 R_2$ and crudely models $\prod_\alpha \delta(I_{1\alpha} - I_{2\alpha})$ where $I_{1\alpha}$ is the Gauss integral between 1 and another, α , by

$$\exp\left(-\int (R_1 - R_2)^2\right) a^{-4} l ds,$$

The entropy of the system is calculated, and in both cases of differentiable and non differentiable chains divergers, but is renormalisable.

Differentiable chains

$$(4.4) \quad S = La^{-2} + qcL \log a + S_0$$

Wiener chains

$$(4.5) \quad S = La^{-2} + pca^{-1} + S_0$$

where q, p are numerical factors and S_0 the rest of the entropy which is logarithmically divergent in (4.4) and a linear divergence in (4.5).

It is possible to extrapolate between these of course because the basic problem is always convergent.⁽¹⁰⁾

5. Conclusion. The difficulty with calculations like that of section 4 is that not only is the calculation tricky, but it is based on very crude topological arguments. However, it appears that the local nature of the chain is more important than the adequacy of the topological invariants.

Finally, it is perhaps worth remarking that dynamics offers a complete evasion of the topological problem but at the high price of needing solutions in time.⁽¹²⁾ The equation of polymers moving in the presence of a fluid is

$$\left(\frac{\partial}{\partial t} - \sum_{\alpha, \beta} \int \int \frac{\partial}{\partial R(s_\alpha)} D(R(s_\alpha) - R(s_\beta)) \left(\frac{\partial}{\partial R(s_\beta)} + \frac{3\partial^2 R_\beta}{l\partial s_\beta^2} \right) \right) P = 0$$

(5.1)

where D is the Oseen tensor (roughly r^{-1}).

It is easy to show such chains cannot cross and so all topological invariants are the invariants of this equation. But I cant solve it.

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ENTROPIC EXPONENTS OF KNOTTED LATTICE POLYGONS

ENZO ORLANDINI*, E.J. JANSE VAN RENSBURG†, MARIA CARLA TESI‡,
AND S.G. WHITTINGTON§

Abstract. Ring polymers in three dimensions can be knotted and the dependence of their critical behaviour on knot type is an open question. We study this problem for self-avoiding polygons on the simple cubic lattice using a novel grand-canonical Monte Carlo algorithm which is a combination of the BFACF algorithm and MMC sampling. We present numerical evidence that the entropic exponent depends on the knot type of the polygon. We conjecture that the exponent increases by unity for each additional factor in the knot factorization of the polygon.

1. Introduction. Polymer molecules in solution are typically very flexible objects which can be highly self-entangled, as well as being entangled with other molecules. It is important to understand and to characterize the extent of this entanglement complexity since it influences crystallization behaviour [1] as well as rheological properties [2]. If a ring closure reaction occurs the entanglement can be trapped as a knot in the resulting ring polymer, and some information about the entanglement complexity can be obtained from a study of the distribution of knots in the ring polymer. In addition, the presence of knots in closed circular DNA can give information about the mechanism of action of enzymes acting on the DNA molecule [3,4,5].

In the last few years some progress has been made towards answering some basic questions about knots, such as discovering the probability that a sufficiently long polymer is knotted [6,7] and the distribution of random knots [8]. However, the statistics of polymer rings with fixed knot type are less well understood. Quantities such as the average size of knotted polymer rings or their configurational entropy (i.e. the number of ways in which such rings can be embedded in space) could in principle depend on the knot type and such dependence can influence the mobility of long polymer chains such as DNA [4]. The question of how the size of a ring polymer depends on its knot type was first addressed by Janse van Rensburg and Whittington [9] by means of Monte Carlo methods. They showed that, although the dimensions of polygons are sensitive to the knot type, the critical exponent ν and the leading amplitude are independent of it. Subsequent studies confirmed the robustness of the critical exponent ν with

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