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Davide Michieletto

Topological Interactions in Ring Polymers

Doctoral Thesis accepted by
the University of Warwick, Coventry, UK

Springer

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ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-3-319-41041-8 ISBN 978-3-319-41042-5 (eBook)
DOI 10.1007/978-3-319-41042-5

Library of Congress Control Number: 2016942899

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG Switzerland

Publications related to this thesis:

(1) D. Michieletto, D. Marenduzzo, E. Orlandini, G.P. Alexander, M.S. Turner, *Threading Dynamics of Ring Polymers in a Gel*, ACS Macro Lett., **3**, 255–259 (2014)

(2) D. Michieletto, D. Marenduzzo, E. Orlandini, G.P. Alexander, M.S. Turner, *Dynamics of Self-Threading Polymers in a Gel*, Soft Matter, **10**, 5936–5944 (2014)

(3) D. Michieletto, E. Orlandini, M.S. Turner, *Rings in Random Environments: Sensing Disorder Through Topology*, Soft Matter, **11**, 1100–1106 (2015)

(4) D. Michieletto, D. Marenduzzo, E. Orlandini, *Is the Kinetoplast DNA a Percolating Network of Linked Rings at its Critical Point?.,* Phys. Biol., **12**, 036001 (2015)

(5) D. Michieletto, D. Marenduzzo, E. Orlandini, *Topological Patterns in Two-dimensional Gel Electrophoresis of DNA Knots*, Proc. Natl. Acad. Sci. USA, **112** (40), E5471–E5477 (2015)

(6) D. Michieletto and M.S. Turner, *A Topologically Driven Glass in Ring Polymers,* Proc. Natl. Acad. Sci. USA, doi:10.1073/pnas.1520665113 (2016)

Supervisor's Foreword

The theoretical methods needed to describe long, flexible polymers started to be developed in the middle of the twentieth century with great names like Flory, Edwards and de Gennes all making important contributions. The arrival of powerful computer simulations in recent decades has allowed us to make further progress by a combination of coarse-graining and either brute-force solution of dynamical equations or ensemble-averaging. Much of the field is now mature and, broadly speaking, the physics of polymers is fairly well understood. However, there is one important island of intellectual difficulty still stubbornly resisting erosion and that is the physics of ring polymers. Rings are polymers that are closed into a long, cyclic macromolecule with no ends and are an important archetype of topological complexity in polymers in general. Ring polymers can be synthesised in the lab or isolated from living systems, such as the plasmids found in bacteria or the exotic chain mail-like genetic material of *Kinetoplastida*. What makes understanding rings difficult is the topological constraint associated with their uncrossability. That is to say that the global topological state of the system at synthesis, with whatever knots and/or links that might then be present, must be maintained for all later times if the polymers cannot break, fuse or cross through one another. An important special case, that is the primary focus of this thesis is that when the polymers all remain unknotted with themselves and unlinked from each other. This is the ensemble most often studied in the literature and, like linear polymers (but in contrast with chain-mail-like topologies), it is ultimately liquid-like, i.e. as it has no zero frequency shear modulus, at least for temperatures above a glass transition temperature, depending (only) on the chain chemistry, below which microscopic molecular motion is lost. What is difficult about topological constraints is that they are highly non-local. If one wants to determine whether two ring polymer conformations are topologically permitted or not, e.g. for inclusion in an ensemble average, one needs information on the entire spatial configuration of both of them. While this makes analytical progress challenging we can still turn to computer simulations.

If one reads the literature from the 80s and 90s one starts to find the first few references of the possibility that inter-ring threadings could occur and that, were

these threading to proliferate, an unusual "tangled" state of matter might arise. This possibility greatly intrigued me when I was still a graduate student in the group at the Cavendish Laboratory in Cambridge led by Sir Sam Edwards. The subsequent development of more efficient computers might partially excuse the fact that it took 20 years for this interest to find an outlet! It is particularly pleasing to see a similar interest in these systems sparked in Davide Michieletto who has produced a thesis that is a *tour de force* for the field. At the risk of sentimentality it is also satisfying to see the baton of polymer theory from the Halcyon days in Cambridge handed down at least one more generation.

This thesis is mainly concerned with computer simulation of unlinked, unknotted ring polymers in various ensembles, these being ring polymers in neutral solvent, ring polymers in perfectly ordered gels and ring polymers in imperfect gels. Why bring gels into the picture? One reason is that they model the environment present in the ubiquitous separation technique known as gel electrophoresis. A more compelling reason is discussed in this thesis: The gel meshwork allows for the formulation of a mathematically precise definition of inter-ring threading, in which one long ring penetrates through another, in much the same way as when one rubber band is threaded through a second; the threaded, or "passive", ring is pinned for as long as the threading, or "active" ring, remains in place. The active ring can diffuse freely while the passive ring can make any (topology-preserving) move provided it does not cross through the active polymer at the site of the penetration. These kinds of threadings have been notoriously difficult to pin down mathematically since, by construction, they do not alter the topological state of the system. It has therefore been difficult to say what the essence of a threading really is and hence which rearrangements produce (or remove) them and which do not.

There are many interesting results in this thesis but, in the interests of keeping this introduction to a modest length, I will focus on the two that were most exciting for me. The first of these is related to exactly this matter—the definition of a threading. Davide's brilliant insight was to use the gel architecture to define cells, through which the rings must lie. When one ring threads a second this alters the topological state of a proxy system: the polymer contours that lie within the cell, truncated at the walls of the cell and then appropriately extended so as to be closed outside the cell. This allows a rigorous definition of threading and, therefore, threading to be counted and tracked in computer simulations of rings moving inside gels. Davide was able to show that threadings do indeed occur and that they proliferate in long rings with a number per ring that appears to be almost exactly proportional to the ring polymer contour length. Combined with evidence for slowing down, due to the requirement that threadings be undone in a particular order, this is perhaps the best evidence to date for the emergence of a highly interpenetrating state in which the longest relaxation times might ultimately scale exponentially in, rather than as a power of, the polymer length. We refer to such a system as a *topological glass* as they would have the extremely unusual property of having exponentially slow (somewhat glassy) relaxation times but show no slowing down in the microscopic dynamics, as the temperature is assumed to remain well above the classical glass transition temperature throughout.

The second really important result in this thesis is concerned with long ring polymers in neutral solvent at high concentrations where the polymer coils are strongly overlapping. Do the threading that were observed in the presence of the gel also occur in this ensemble? A new approach was required as the gel is no longer present and its architecture cannot therefore be exploited as before. Davide's second really brilliant insight was to realise that threading can be identified by artificially immobilising ("freezing") a fraction of the ring polymers in an equilibrated simulation of rings so that they have no microscopic freedom to move at all. If threading are present then some of them will involve a ring in the frozen fraction threading through one that is unfrozen. In this case the unfrozen chain will effectively experience a permanent threading and be pinned at the site of that threading throughout the simulation. The pinned chain can still move but can only diffuse away a distance that is of the order of the equilibrium coil size as the pinning delivered by the frozen ring must remain somewhere within its contour. Davide then showed that such confined diffusion can be observed in these systems of rings and, by construction that such threading would have been present, at least transiently, in the equilibrated system prior to (partial) freezing. This essentially proves, for the first time, the existence of threadings in concentrated ring systems and opens up an entire field of study concerned with the properties of these threaded systems and the topological glass that might eventually emerge from them.

Coventry, UK
April 2016

Prof. Matthew S. Turner

Abstract

Ring polymers offer a richness of behaviours that are of broad interest and have deep consequences in many fields of Science. In this thesis I investigate some general and universal properties, i.e. independent of the chemical nature of the polymers, emerging from systems made of a collection of rings. These will be studied by using methods of equilibrium and non-equilibrium Statistical Mechanics together with Molecular Dynamics simulations of coarse-grained models for the systems under investigation. Within these frameworks, important questions regarding the macroscopic behaviour of ring-shaped polymers have yet to find a satisfactory answer. The work presented in this Thesis finds its principal motivations in problems arising in Material Science, the so-called "melt" of rings, and in Biology, such as the organisation of mitochondrial DNA in some organisms and the mechanisms governing the electrophoretic separation of DNA samples in gels. There are several theoretical challenges in these fields which represent state-of-the-art scientific research and whose partial answers are provided in the work presented in this Thesis. One of the major achievements of the work presented is the general understanding of the role played by topological properties, i.e. those invariant under smooth deformations of the polymer contour, on the macroscopic behaviour of the investigated systems. Finally, the conclusions drawn from the presented work can have important scientific consequences as they may ultimately lead to a more complete understanding of complicated issues in Biology and to the design of next-generation soft materials.

Acknowledgments

There is a number of people that I would like to thank and for a number of reasons. It is very likely that the following acknowledgements will not do justice to all of them, but I will try.

I believe that the first to be thanked, both emotionally and chronologically, should be my family. No matter the difficulties and preoccupations throughout the (long) period of my education, they always offered their indefatigable support, and for that I am glad and grateful. I would like to thank in particular my parents, grandparents and uncles who spent a considerable part of their life with me since when I was very young and had therefore shaped my character and attitude towards life. I am satisfied with the person that I have become and I owe a big part of this to you.

Second, I would like to warmly thank Stefania for her talent to bring out the best in me. You have a mysterious ability of being both, a pillow to my mind and a fire that kindles my soul and that drives me towards new goals and adventures. I most certainly would not be the person I am if it wasn't for you, and I am exceedingly pleased that you have become my best friend and partner since very early in my life.

I would also like to thank the many brilliant persons who I am honoured to call friends. I am glad that the physical distance separating us has not weakened our bonds.

Finally, I would like to thank my supervisor Matthew for his supporting and always too kind words throughout the Ph.D.; Gareth for having taught me to look for the beauty in all the little things; Davide and Enzo for their positive and constant support and for acting not only as mentors but also as friends and fellow countrymen. I thank all of them for sharing their time and precious insight when I was in need of ideas and seeking inspiration.

Contents