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Saint-Flour Probability Summer School

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Jean Picard
Summer School Chairman
Laboratoire de Mathématiques
Université Blaise Pascal
63177 Aubière Cedex
France

Frank den Hollander

Random Polymers

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Frank den Hollander
University of Leiden
Department of Mathematics
Niels Bohrweg 1
2333 RA Leiden
The Netherlands
denholla@math.leidenuniv.nl

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Preface

This monograph contains the worked out and expanded notes of the lecture series I presented at the 37–th Probability Summer School in Saint-Flour, 8–21 July 2007. The goal I had set myself for these lectures was to provide an up-to-date account of some key developments in the *mathematical* theory of polymer chains, focusing on a number of models that are at the heart of the subject. In order to achieve this goal, I decided to limit myself to single polymers living on a lattice, to consider only models for which a transparent picture has emerged, and from the latter select those that lead to challenging open questions capable of attracting future research. Needless to say, my choice was influenced by my personal taste and involvement.

Polymers are studied intensively in mathematics, physics, chemistry and biology. Our focus will lie at the interface between *probability theory* and *equilibrium statistical physics*. To fully appreciate the results to be described, the reader needs a basic knowledge of both these areas. No other background is required. We will look at a number of *paradigm* models that exhibit interesting phenomena. The key objects of interest will be free energies, phase transitions as a function of underlying parameters and associated critical behavior, scaling properties of path measures in the different phases and associated invariance principles, as well as effects of randomness in the interactions. The emphasis will be on techniques coming from large deviation theory, combinatorics, ergodic theory and variational calculus.

We start with two basic models of polymer chains: *simple random walk* and *self-avoiding walk*. After having collected a few key properties of these models, which serve to set the stage, we turn to the main body of the monograph, which is divided into two parts.

In Part A, we look at four models of polymers with self-interaction: (1) *soft polymers*, where self-intersections are not forbidden but are penalized, resulting in a repulsive interaction modeling the effect of "steric hindrance"; (2) *elastic polymers*, where self-intersections are penalized in a way that depends on their distance along the chain, in such a way that long loops are less penalized than short loops; (3) *polymer collapse*, where due to attractive

interactions the polymer may roll itself up to form a ball; (4) *polymer adsorption*, where the polymer interacts with a linear substrate to which it may be attracted, either moving on both sides of the substrate (pinning at an interface) or staying on one side of the substrate (wetting of a surface).

In PART B, we look at five models of POLYMERS IN RANDOM ENVIRONMENT: (1) *charged polymers*, where positive and negative charges are arranged randomly along the chain, resulting in a mixture of repulsive and attractive interactions; (2) *copolymers near a linear selective interface*, where the polymer consists of a random concatenation of two types of monomers that interact differently with two solvents separated by a linear interface; (3) *copolymers near a random selective interface*, where the linear interface is replaced by a percolation-type interface; (4) *random pinning and wetting of polymers*, where the polymer interacts with a linear interface or surface consisting of different types of atoms or molecules arranged randomly; (5) *polymers in a random potential*, where the polymer interacts with different types of atoms or molecules arranged randomly in space.

All the results that are presented come with a complete mathematical proof. Nonetheless, there are a few places where proofs are a bit sketchy and the reader is referred to the literature for further details. Not doing so would have meant lengthening the exposition considerably. Still, even where proofs are tight I have taken care that the reader can always hold on to the main line of the argument.

All chapters can be read *essentially independently*. Each chapter tells a story that is *self-contained*, both in terms of content and of notation. Each chapter ends with a brief description of a number of important *extensions* (added to further enlarge the panorama) and with a number of *challenges* for the future (ranging from "doable in principle" via "very tough indeed" to "almost beyond hope"). An index with key words is added after the references, to help the reader connect the terminology that is used in the different chapters. For the topics covered in Parts A and B, I believe to have caught most of the relevant *mathematical* literature. There is a huge literature in physics and chemistry, of which only a few snapshots are being offered.

The choice I made of what material to cover was not driven by content alone. I also wanted to exhibit a number of key techniques that are currently available in the area and are being developed further. Thus, the reader will encounter the *method of local times* (Chapters 3, 6 and 8), *large deviations* and *variational calculus* (Chapters 3, 6, 9 and 10), the *lace expansion* in combination with the *induction approach* (Chapters 4 and 5), *generating functions* (Chapters 6 and 7), the *method of excursions* (Chapters 7, 9 and 11), the *subadditive ergodic theorem* (Chapters 9, 10 and 11), *partial annealing estimates* (Chapters 9, 10 and 11), *coarse-graining* (Chapter 10), and *martingales* (Chapter 12).

I greatly benefited from reading overview works that address various *mathematical* aspects of polymers, in particular, the monographs by Barber and Ninham [12], Madras and Slade [230], Hughes [175], Vanderzande [300],

van der Hofstad [154], Sznitman [288], Janse van Rensburg [188], Slade [280], and Giacomin [116], the review papers by van der Hofstad and König [165], Bolthausen [28], and Soteros and Whittington [283], as well as the PhD theses of Caravenna [51], Pétrélis [263], and Vargas [302]. If the present monograph contributes towards making the area more accessible to a broad mathematical readership, as the above works do, then I will consider my goal reached.

While planning this monograph, I decided not to touch upon combinatorial counting techniques, exact enumeration methods and power series analysis, which provide invaluable insight for models that are too hard to handle analytically. Nor will the reader find a description of knotted polymers, which have many fascinating properties and a broad range of applications, nor of branched polymers, which are related to superprocesses arising as scaling limit. These are rapidly growing subjects, which the reader is invited to explore. For overviews, see Dušek [93], Guttmann [137], Orlandini and Whittington [257], and Guttmann [138]. Similarly, there is no discussion of models of two or more polymers interacting with each other, like in a polymer melt, nor of models dealing with dynamical aspects of polymers, such as reptation in a polymer melt. For overviews, see de Gennes [114], and Doi and Edwards [92]. The literature offers plenty of possibilities for the latter two topics as well, but so far the mathematics is rather thin.

I am grateful to Marek Biskup, Erwin Bolthausen, Andreas Greven, Remco van der Hofstad, Wolfgang König, Nicolas Pétrélis, Gordon Slade, Stu Whittington and Mario Wüthrich for co-authoring the joint papers we wrote on random polymers and for the many interesting and enjoyable discussions we have shared over the years. I am further grateful to Anton Bovier, Matthias Birkner, Thierry Bodineau, Francesco Caravenna, Francis Comets, Giambattista Giacomin, Tony Guttmann, Neil O'Connell, Andrew Rechnitzer, Chris Soteros, Alain-Sol Sznitman, Fabio Toninelli, Ivan Velenik and Lorenzo Zambotti for fruitful exchange on various occasions.

Matthias Birkner, Giambattista Giacomin, Remco van der Hofstad and Gordon Slade read parts of the prefinal draft and offered a number of useful remarks. Stu Whittington commented on three drafts in various stages of development, patiently answered a long list of questions and provided many references. He generously offered his guidance, which has been both stimulating and reassuring. Nicolas Pétrélis helped me to prepare my lectures in Saint-Flour and assisted me afterwards to finish the present monograph. Not only did we spend many hours together discussing the content, Nicolas carefully went through the full text and drew many of the figures. He was an indispensable companion in bringing the whole enterprise to a good end.

It is a pleasure to thank the staff of EURANDOM in Eindhoven for providing so many opportunities to do quiet research in a stimulating environment. It continues to be an honor and a pleasure to be affiliated with the institute, where most of the above colleagues are at home. Over the years, my research has been amply supported by NWO (Netherlands Organization for Scientific Research), which I gratefully acknowledge as well.

Finally, I thank Jean Picard for the invitation to lecture at the Saint-Flour summer school and for the pleasant exchange we have had before, during and after the event.

Frank den Hollander

Mathematical Institute
Leiden University
P.O. Box 9512
2300 RA Leiden
The Netherlands
www.math.leidenuniv.nl/∼denholla/
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