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Random Polymers

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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 Giacomini [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], Guttman [137], Orlandini and Whittington [257], and Guttman [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 Giacomini, Tony Guttman, 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 Giacomini, 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.

VIII Preface

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.

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Contents

1	Introduction	1
1.1	What is a Polymer?	1
1.2	What is the Model Setting?.....	3
1.3	The Central Role of Free Energy	6
2	Two Basic Models	9
2.1	Simple Random Walk	9
2.2	Self-avoiding Walk	12

Part A Polymers with Self-interaction

3	Soft Polymers in Low Dimension	19
3.1	A Polymer with Self-repelling	19
3.2	Weakly Self-avoiding Walk in Dimension One	20
3.3	The Large Deviation Principle for Bridges	22
3.4	Program of Five Steps	25
3.4.1	Step 1: Adding Drift	25
3.4.2	Step 2: Markovian Nature of the Total Local Times	26
3.4.3	Step 3: Key Variational Problem	27
3.4.4	Step 4: Solution of the Variational Problem in Terms of an Eigenvalue Problem	30
3.4.5	Step 5: Identification of the Speed	33
3.5	The Large Deviation Principle without the Bridge Condition	34
3.6	Extensions	35
3.7	Challenges	37
4	Soft Polymers in High Dimension	41
4.1	Weakly Self-avoiding Walk in Dimension Five or Higher ...	41
4.2	Expansion	43
4.2.1	Graphs and Connected Graphs	43
4.2.2	Recursion Relation	45

4.3	Laces	46
4.3.1	Laces and Compatible Edges	46
4.3.2	Resummation	48
4.4	Diagrammatic Estimates	49
4.5	Induction	51
4.5.1	Notation	51
4.5.2	Heuristics	52
4.5.3	Induction Hypotheses	53
4.6	Proof of Diffusive Behavior	54
4.7	Extensions	56
4.8	Challenges	58
5	Elastic Polymers	59
5.1	A Polymer with Decaying Self-repulsion	59
5.2	The Lace Expansion Carries over	60
5.3	Extensions	61
5.4	Challenges	63
6	Polymer Collapse	67
6.1	An Undirected Polymer in a Poor Solvent	67
6.1.1	The Minimally Extended Phase	69
6.1.2	The Localized Phase	70
6.1.3	Conjectured Phase Diagram	73
6.2	A Directed Polymer in a Poor Solvent	74
6.2.1	The Collapse Transition	76
6.2.2	Properties of the Two Phases	80
6.3	Extensions	81
6.4	Challenges	83
7	Polymer Adsorption	85
7.1	A Polymer Near a Linear Penetrable Substrate: Pinning ...	86
7.1.1	Free Energy	88
7.1.2	Path Properties	91
7.1.3	Order of the Phase Transition	93
7.2	A Polymer Near a Linear Impenetrable Substrate: Wetting	93
7.3	Pulling a Polymer off a Substrate by a Force	95
7.3.1	Force and Pinning	96
7.3.2	Force and Wetting	99
7.4	A Polymer in a Slit between Two Impenetrable Substrates	101
7.4.1	Model	101
7.4.2	Generating Function	103
7.4.3	Effective Force	104
7.5	Adsorption of Self-avoiding Walks	106
7.6	Extensions	107
7.7	Challenges	111

Part B Polymers in Random Environment

8	Charged Polymers	115
8.1	A Polymer with Screened Random Charges	116
8.2	Scaling of the Free Energy	117
8.2.1	Variational Characterization	117
8.2.2	Heuristics	119
8.2.3	Large Deviations	121
8.3	Subdiffusive Behavior	121
8.4	Parabolic Anderson Equation	122
8.5	Extensions	123
8.6	Challenges	126
9	Copolymers Near a Linear Selective Interface	129
9.1	A Copolymer Interacting with Two Solvents	130
9.2	The Free Energy	132
9.3	The Critical Curve	135
9.3.1	The Localized and Delocalized Phases	135
9.3.2	Existence of a Non-trivial Critical Curve	136
9.4	Qualitative Properties of the Critical Curve	138
9.4.1	Upper Bound	138
9.4.2	Lower Bound	138
9.4.3	Weak Interaction Limit	141
9.5	Qualitative Properties of the Phases	142
9.5.1	Path Properties	143
9.5.2	Order of the Phase Transition	143
9.5.3	Smoothness of the Free Energy in the Localized Phase	145
9.6	Extensions	147
9.7	Challenges	153
10	Copolymers Near a Random Selective Interface	155
10.1	A Copolymer Diagonally Crossing Blocks	156
10.2	Preparations	158
10.2.1	Variational Formula for the Free Energy	158
10.2.2	Path Entropies	161
10.2.3	Free Energies per Pair of Blocks	162
10.2.4	Percolation	164
10.3	Phase Diagram in the Supercritical Regime	165
10.3.1	Free Energy in the Two Phases	166
10.3.2	Criterion for Localization	167
10.3.3	Qualitative Properties of the Critical Curve	169
10.3.4	Finer Details of the Critical Curve	173

10.4	Phase Diagram in the Subcritical Regime.....	175
10.5	Extensions.....	177
10.6	Challenges.....	178
11	Random Pinning and Wetting of Polymers	181
11.1	A Polymer Near a Linear Penetrable Random Substrate: Pinning	182
11.2	The Free Energy	183
11.3	The Critical Curve	184
11.3.1	The Localized and Delocalized Phases	184
11.3.2	Existence of a Non-trivial Critical Curve	184
11.4	Qualitative Properties of the Critical Curve.....	185
11.4.1	Upper Bound	185
11.4.2	Lower Bound	186
11.4.3	Weak Interaction Limit	190
11.5	Qualitative Properties of the Phases	191
11.6	Relevant versus Irrelevant Disorder	191
11.7	A Polymer Near a Linear Impenetrable Random Substrate: Wetting	194
11.8	Pulling a Polymer off a Substrate by a Force.....	195
11.8.1	Force and Pinning	196
11.8.2	Force and Wetting.....	197
11.9	Extensions.....	198
11.10	Challenges.....	204
12	Polymers in a Random Potential	205
12.1	A Homopolymer in a Micro-emulsion	206
12.2	A Dichotomy: Weak and Strong Disorder	207
12.2.1	Key Martingale	207
12.2.2	Separation of the Two Phases	209
12.2.3	Characterization of the Two Phases	209
12.2.4	Diffusive versus Non-diffusive Behavior.....	211
12.2.5	Bounds on the Critical Temperature	211
12.3	Proof of Uniqueness of the Critical Temperature.....	212
12.4	Martingale Estimates	214
12.4.1	First Estimate	215
12.4.2	Second Estimate	218
12.5	The Weak Disorder Phase	220
12.6	The Strong Disorder Phase	220
12.7	Beyond Second Moments	221
12.7.1	Fractional Moment Estimates	222
12.7.2	Size-biasing.....	223
12.7.3	Relation with Random Pinning	225

12.8 Extensions	226
12.9 Challenges	230
References	233
Index	249
List of Participants	253
Programme of the School	257