Lecture Notes in Mathematics

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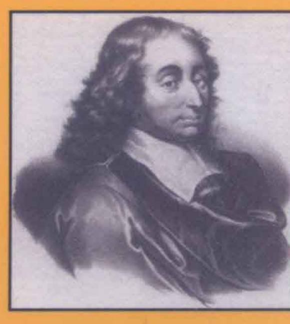
Frank den Hollander

Random Polymers

École d'Été de Probabilités
de Saint-Flour XXXVII – 2007



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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.

Mathematical Institute
Leiden University
P.O. Box 9512
2300 RA Leiden
The Netherlands
www.math.leidenuniv.nl/~denholla/
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Frank den Hollander

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Part B Polymers in Random Environment

1

Introduction

1.1 What is a Polymer?

A *polymer* is a large molecule consisting of *monomers* that are tied together by chemical bonds. The monomers can be either small units (such as CH_2 in polyethylene; see Fig. 1.1) or larger units with an internal structure (such as the adenine-thymine and cytosine-guanine base pairs in the DNA double helix; see Fig. 1.2). Polymers abound in nature because of the *multivalency* of atoms like carbon, silicon, oxygen, nitrogen, sulfur and phosphorus, which are capable of forming long concatenated structures.

Polymer Classification. Polymers come in two varieties: (1) HOMOPOLYMERS, with all their monomers identical (such as polyethylene); (2) COPOLYMERS, with two or more different types of monomer (such as DNA). The order of the monomer types in copolymers can be either periodic (e.g. in agar) or random (e.g. in carrageenan).

An important classification of polymers is into SYNTHETIC POLYMERS (such as nylon, polyethylene and polystyrene) and NATURAL POLYMERS (also called biopolymers). Major subclasses of the latter are: (a) *proteins* (strings of amino-acids), the chief constituents of all living objects, carrying out a multitude of tasks; (b) *nucleic acids* (DNA, RNA), the building blocks of genes that are the very core of life processes; (c) *polysaccharides* (e.g. agar, amylose, carrageenan, cellulose), which form part of the structure of animals and plants and provide an energy source; (d) *lignin* (plant cement), which fills up the space between cellulose fibres; (e) *rubber*, occurring in the fluid of latex cells in certain trees and shrubs. Apart from (a)–(e), which are *organic* materials, clays and minerals are *inorganic* examples of natural polymers. Synthetic polymers typically are homopolymers, natural polymers typically are copolymers (with notable exceptions). Bacterial polysaccharides tend to be periodic, plant polysaccharides tend to be random.

Yet another classification of polymers is into LINEAR and BRANCHED. In the former, the monomers have one reactive group (such as CH_2), leading

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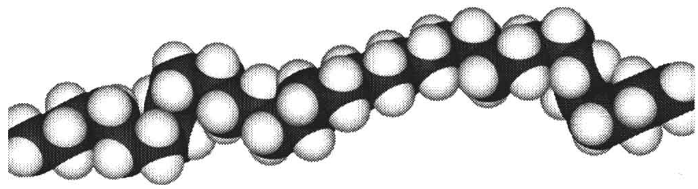

Fig. 1.1. Polyethylene.

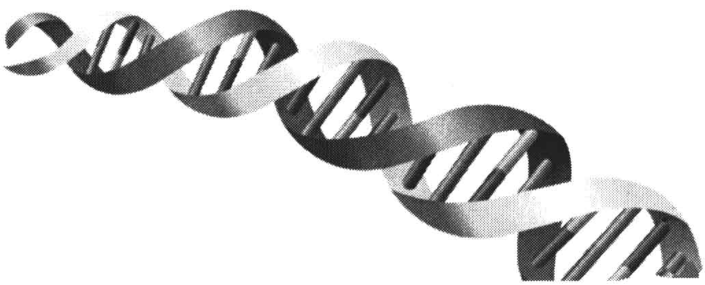

Fig. 1.2. DNA.

to a linear organization as a result of the polymerization process. In the latter, the monomers have two or more reactive groups (such as hydroxy acid), leading to an intricate network with multiple cross connections. Most natural polymers are linear, like DNA, RNA, proteins and the polysaccharides agar, alginate, amylose, carrageenan and cellulose. Some polysaccharides are branched, like amylopectin. Many synthetic polymers are linear, and many are branched. An example of a branched polymer is rubber, both natural and synthetic.

Polymerization. The chemical process of building a polymer from monomers is called *polymerization*. The size of a polymer, i.e., the number of constituent monomers (also called the degree of polymerization) may vary from 10^3 up to 10^{10} (smaller molecules do not qualify to be called polymers, larger molecules have not been recorded). Human DNA has $10^9 - 10^{10}$ base pairs, lignin consists of $10^6 - 10^7$ phenyl-propanes, while polysaccharides carry $10^3 - 10^4$ sugar units. Both in synthetic and in natural polymers, the size distribution may either be broad, with numbers varying significantly from polymer to polymer (e.g. in nylons and in polysaccharides) or be narrow (e.g. in proteins and in DNA). In synthetic polymers the size distribution can be made narrow through specific polymerization methods. The size of the monomer units varies from 1.5 Å (for CH_2 in polyethylene) to 20 Å (for the base pairs in DNA), with $1\,\text{Å} = 10^{-10}\,\text{m}$. For more background on the structure of polymers, the reader is referred to Green and Milne [129].

The chemical bonds in a polymer are flexible, so that the polymer can arrange itself in many different *spatial configurations*. The longer the chain, the more involved these configurations tend to be. For instance, the polymer can wind around itself to form knots, can be extended due to repulsive forces between the monomers as a result of excluded-volume, or can collapse to a ball due to attractive van der Waals forces between the monomers or repulsive forces between the monomers and a poor solvent. It can also interact with a surface on which it may or may not be adsorbed, or it can live in a slit between two confining surfaces.

As mentioned above, the polymer can be either homogeneous (homopolymer) or inhomogeneous (copolymer). A typical example of the latter is a copolymer whose monomers carry positive and negative charges, randomly arranged along the chain. Another example is a copolymer consisting of hydrophobic and hydrophilic monomers. If such a copolymer is placed near an interface separating oil and water, then it may try to wiggle around the interface in order to match the monomers as much as possible, and in doing so stay closely tied to the interface.

Targets. In the present monograph we will consider various different models of *linear* polymers, aimed at describing a variety of different physical settings, of the type alluded to above. Key quantities of interest will be the number of different spatial configurations, the typical end-to-end distance (subdiffusive, diffusive or superdiffusive), the space-time scaling limit, the fraction of monomers at an interface or adsorbed onto a surface, the average length and height of excursions away from an interface or a surface, all typically in the limit as the polymer gets long. We will pay special attention to the free energy of the polymer in this limit, and to the presence of *phase transitions* as a function of underlying model parameters, signalling drastic changes in behavior when these parameters cross critical values. We will also study the effect of randomness in the interactions.

Classical monographs on polymers with a physical and chemical orientation are Flory [102] and de Gennes [114]. (It is worthwhile to read their Nobel lectures: Flory [103] and de Gennes [115].) Monographs with a mathematical orientation are Barber and Ninham [12], Madras and Slade [230], Hughes [175], Vanderzande [300], Janse van Rensburg [188] and Giacomin [116].

1.2 What is the Model Setting?

Our polymers will live on the d-dimensional Euclidean lattice $\mathbb{Z}^d$, $d \geq 1$. They will be modelled as *random paths* on this lattice, where the monomers are the vertices in the path, and the chemical bonds connecting the monomers are the edges in the path.

The choice of model will depend on two key objects. Namely, for each $n \in \mathbb{N}_0 = \mathbb{N} \cup \{0\}$ we need to specify

$$\begin{aligned} \mathcal{W}_n &= \text{a collection of allowed } n\text{-step } \textit{paths} \text{ on } \mathbb{Z}^d, \\ H_n &= \text{a Hamiltonian that associates an } \textit{energy} \text{ to each path in } \mathcal{W}_n. \end{aligned} \tag{1.1}$$

As we will see, there is flexibility in the choice of $\mathcal{W}_n$, depending on the particular application we have in mind. We will be considering both undirected and directed paths (see Figs. 1.3 and 1.4). The choice of H_n will be driven by the underlying physics, and captures the interaction of the polymer with itself and/or its environment. Typically, H_n depends on one or two parameters, including temperature.

For each $n \in \mathbb{N}_0$, the *random polymer* of length n is defined by assigning to each $w \in \mathcal{W}_n$ a probability given by

$$P_n(w) = \frac{1}{Z_n} \mathrm{e}^{-H_n(w)}, \qquad w \in \mathcal{W}_n, \tag{1.2}$$

where Z_n is the normalizing partition sum. This is called the *Gibbs measure* associated with the pair $(\mathcal{W}_n, H_n)$, and it describes the polymer in *equilibrium* with itself and/or its environment (at fixed temperature and fixed polymer

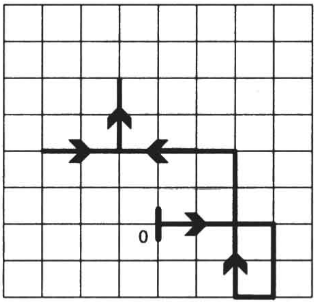

Fig. 1.3. A 19-step path on $\mathbb{Z}^2$, modeling a polymer in the plane with 20 monomers tied together by 19 chemical bonds. The steps in the path are: 3 east, 2 south, 1 west, 4 north, 5 west, 2 east and 2 north.

Fig. 1.4. Three examples of directed paths on $\mathbb{Z}^2$, in combinatorics commonly referred to as ballot paths (with allowed steps $\nearrow$ or $\searrow$), generalized ballot paths (with allowed steps $\nearrow$, $\rightarrow$ and $\searrow$), and partially directed self-avoiding walks (with allowed steps $\uparrow$, $\downarrow$ or $\rightarrow$, subject to no self-intersections). Ballot paths and generalized ballot paths that begin and end at the same horizontal line and lie entirely on or above this line are called Dyck paths, repectively, Motzkin paths. Without the one-sidedness restriction they are called bilateral Dyck paths, respectively, bilateral Motzkin paths.

length). Under this Gibbs measure, paths with a low energy have a high probability, while paths with a high energy have a low probability.[1]

Note that $(P_n)_{n\in\mathbb{N}}$ in general is *not* a consistent family of probability distributions, i.e., P_n is not the projection of P_{n+1} obtained by summing out the position of the $(n+1)$-st monomer. Rather, for each n we have a different distribution, modeling a polymer chain of a fixed length.

The polymer measure in (1.2) will be our main focus in PART A. In PART B we will consider models in which the Hamiltonian also depends on a *random environment* (e.g. randomly ordered charges or monomer types). We will generically denote this random environment by ω and its probability distribution by $\mathbb{P}$. We will write H_n^ω to exhibit the ω-dependence of the Hamiltonian. Three types of Gibbs measures will make their appearance:

(1) The *quenched* Gibbs measure

$$P_n^\omega(w) = \frac{1}{Z_n^\omega}\, \mathrm{e}^{-H_n^\omega(w)}, \qquad w \in \mathcal{W}_n. \tag{1.3}$$

(2) The *average quenched* Gibbs measure

$$\mathbb{E}(P_n^\omega(w)) = \int P_n^\omega(w)\, \mathbb{P}(\mathrm{d}\omega), \qquad w \in \mathcal{W}_n. \tag{1.4}$$

(3) The *annealed* Gibbs measure

$$\mathbb{P}_n(w) = \frac{1}{\mathbb{Z}_n} \int \mathrm{e}^{-H_n^\omega(w)}\, \mathbb{P}(\mathrm{d}\omega), \qquad w \in \mathcal{W}_n. \tag{1.5}$$

The latter is used to model a polymer whose random environment is not frozen but takes part in the equilibration. We will mostly be interested in the behavior of the polymer in the limit as $n \to \infty$, typically after some appropriate scaling.[2]

We will not (!) consider models where the length or the configuration of the polymer changes with time (e.g. due to growing or shrinking, or to a Metropolis dynamics associated with the Hamiltonian for an appropriate choice of allowed transitions). These *non-equilibrium* situations are very interesting and challenging indeed, but so far the available mathematics is very thin.

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[1] W. Kuhn, in the 1930's, seems to have been the first to put forward the "ensemble description" of polymers given by (1.2) (see Flory [100], Chapter I). The Gibbs measure in (1.2) maximizes the *entropy* $\sum_{w\in\mathcal{W}_n}[-P_n(w)\log P_n(w)]$ subject to the constraint of constant *energy* $\sum_{w\in\mathcal{W}_n} P_n(w)H_n(w)$, as required by equilibrium statistical physics.

[2] The reader must carefully distinguish between the upper index ω, labeling the random environment, and the argument w, labeling the path, even though these symbols look very much alike. In Part B they will appear side by side in many formulas.