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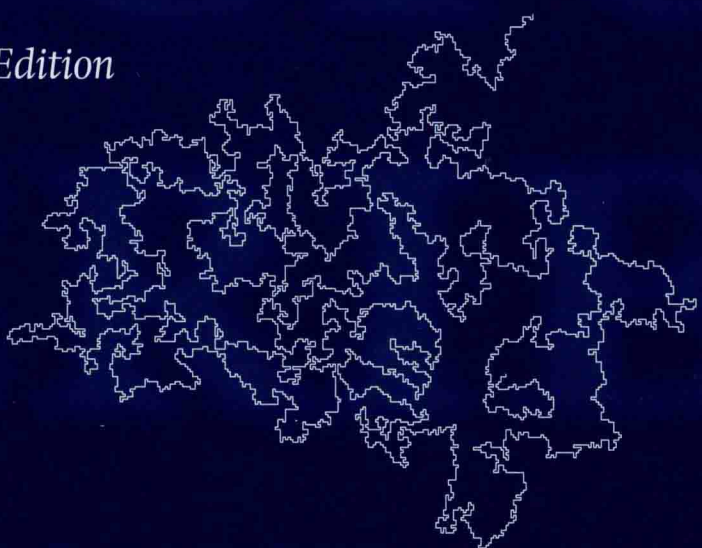
2nd Edition



E.J. Janse van Rensburg

The Statistical Mechanics of Interacting Walks, Polygons, Animals and Vesicles

Second Edition

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Dedicated to the women in my life: Katherine, my mother Lenie, my Daughters, Sister and Grandmothers, who have given much and taken little in return.

PREFACE

The central topic of this book is the modelling of polymer entropy on lattices. This is a classical field of lattice statistical mechanics models which include the self-avoiding walk, lattice trees and animals, and lattice surfaces. The analysis of lattice models of polymer entropy is fundamentally a combinatorial problem, namely, the counting of connected structures in a lattice. Many lattice models remain intractable and can only be analysed using sophisticated mathematical approaches.

Lattice models of the self-avoiding walk, or clusters such as lattice trees and animals, vesicles and surfaces, may be directed or undirected, interacting or free, confined in sub-lattices or interacting with a boundary. In each case the basic questions are similar in nature, namely, how many walks, paths or clusters are there of given size, what are the free energies, what are the scaling properties and can anything be said about the phase diagrams?

Determining the free energies and phase diagrams of lattice models poses in most cases challenging mathematical problems. A wide collection of approaches, including methods from mathematical physics, probability theory, combinatorics and the theory of phase transitions, has been used in some way or another in the very large scientific literature devoted to these models. Numerical approaches have become equally sophisticated and are for the most part based on exact enumeration or Monte Carlo methods.

The free energy of a lattice model defines its phase diagram, which may include several phases separated by critical lines and points. The phases are frequently representative of phase behaviour seen in polymeric systems, and universal thermodynamic scaling near critical points remains the subject of much research. Proving the existence of phase boundaries and critical points and calculating critical exponents pose significant difficulties in many models. It is both the mathematical challenges and the significant progress made which underlie the continuing popularity of lattice models of polymeric systems. Much has been shown, and even more remains to be discovered and seems within reach.

The first edition of this book was out of date within a few years of its publication in the year 2000, due to the fast pace of new results. This, and the omission of a chapter on Monte Carlo methods, made an update of the first edition a priority, and I hope that the new edition will improve on the first.

An undertaking of this size draws on the resources of many, and I have benefited and learned much over two decades in collaborations with Stuart Whittington, Enzo Orlandini, Carla Tesi, Andrew Rechnitzer, Claus Ernst, Yuanan Diao and Neal Madras. I am also grateful to Emmanuel Bradlow for his support more than thirty years ago, and to Ron Horgan for introducing me to the ideas and models in polymer entropy.

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DETAILED CONTENTS

1

LATTICE MODELS OF LINEAR AND RING POLYMERS

A linear polymer is a large molecule consisting of a backbone of atoms or groups of atoms (monomers) which are joined in a sequence by covalent bonds. Parts of a polymer joined by a single covalent bond may rotate freely relative to one another, since single covalent bonds permit free rotations. These rotational degrees of freedom contribute to the configurational entropy of the polymer – quantifying this configurational entropy is the fundamental problem in polymer entropy [117, 202–204].

A typical polymer is illustrated in figure 1.1. If all the monomers are chemically identical, then the polymer is a *homopolymer*, and, if they are of at least two different flavours, then it is a *heteropolymer*.

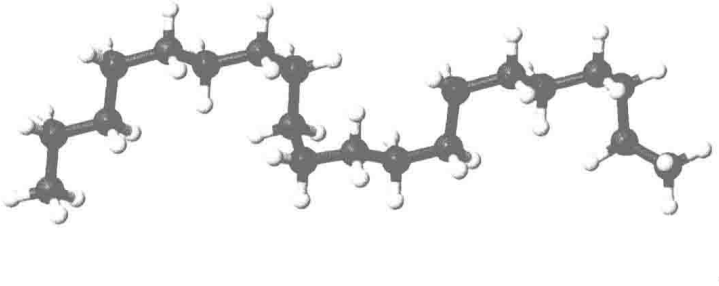

FIG. 1.1. An alkane with a backbone of twenty carbon atoms bound in a linear chain [600].

A *branched polymer* is formed when polymeric side-chains are attached to a polymer *backbone*. Branched polymers are found in different forms, including *trees* and *animals*, as well as *brushes, combs, stars, dendrimers*, and so on.

A popular model of linear polymer entropy is a random walk (see for example reference [176]). A random walk is a good model for the conformational degrees of freedom but fails to explain the asymptotic properties of a linear polymer in a good solvent because *excluded volume effects* are not included in the model.

Configurational entropy and excluded volume of a linear polymer can be modelled by a lattice *self-avoiding walk*. A self-avoiding walk is the union of a sequence of lattice edges or steps joining adjacent vertices along a path which

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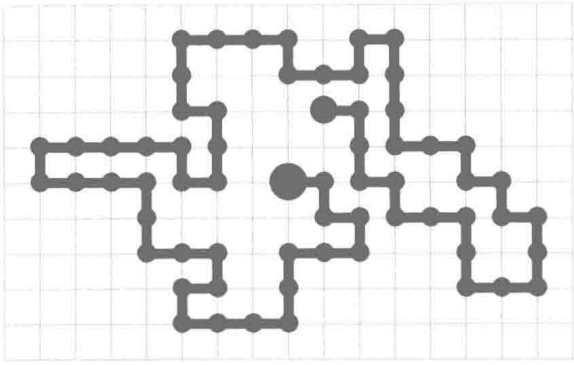

FIG. 1.2. A self-avoiding walk from the origin in $\mathbb{L}^2$. The walk is oriented away from its endpoint at the origin.

avoids itself. The number of such paths is the microcanonical partition function in the model and is a quantitative and relative measure of linear polymer entropy.

The self-avoiding walk model is obtained by endowing the set of self-avoiding walks of fixed given length with the uniform measure. This is a classical model about which a great deal is known and even more remains unknown [399].

1.1 The self-avoiding walk

Let $\mathbb{R}^d$ be d-dimensional real vector space and denote its standard basis by $\langle \vec{e}_1, \vec{e}_2, \ldots, \vec{e}_d \rangle$. The *hypercubic lattice* $\mathbb{L}^d$ is the graph $\mathbb{R}^d$ with vertex set $\mathbb{Z}^d$ and edge set formed by all unit length line segments between vertices in $\mathbb{Z}^d$. That is,

$$\mathbb{L}^d = \big\{ \langle \vec{v} \sim \vec{u} \rangle \mid \text{for } \vec{u}, \vec{v} \in \mathbb{L}^d \text{ with } \|\vec{u} - \vec{v}\|_2 = 1 \big\}. \tag{1.1}$$

If $\langle \vec{u} \sim \vec{v} \rangle \in \mathbb{L}^d$, then $\vec{u}, \vec{v} \in \mathbb{L}^d$ and $\vec{u}$ and $\vec{v}$ are *adjacent* while $\vec{u}$ (or $\vec{v}$) is *incident* with $\langle \vec{u} \sim \vec{v} \rangle$. If $\vec{v} \in \mathbb{L}^d$ is a vertex, then its Cartesian coordinates are $\langle \vec{v}(1), \vec{v}(2), \ldots, \vec{v}(d) \rangle$.

A *self-avoiding walk* ω of length n steps is a sequence of $n+1$ distinct vertices $\langle \vec{v}_i \rangle_{i=0}^{n} = \langle \vec{v}_0, \vec{v}_1, \vec{v}_2, \ldots, \vec{v}_n \rangle$ such that $\langle \vec{v}_{i-1} \sim \vec{v}_i \rangle$ is an edge in $\mathbb{L}^d$ for $i = 1, 2, \ldots, n$. The i-th edge in the walk is $\langle \vec{v}_{i-1} \sim \vec{v}_i \rangle$. Normally, the zeroth vertex is placed at the origin: $\vec{v}_0 = \vec{0}$. This induces a natural orientation in each walk, away from $\vec{0}$ (see figure 1.2).

The number of self-avoiding walks from $\vec{0}$ of length n is denoted by c_n. It can be checked that $c_0 = 1$ (a single vertex), and in $\mathbb{L}^d$, $c_1 = 2d$, $c_2 = 2d(2d-1)$, and $c_3 = 2d(2d-1)^2$. If $d = 2$, then $c_4 = 100$, and $c_5 = 284$. Notice that $c_{n+1} \leq (2d-1)c_n$ for $n \geq 1$, since there are at most $2d-1$ choices for the $(n+1)$-th step. This shows that $c_n \leq 2d(2d-1)^{n-1}$. By counting walks which only step in positive directions, $c_n \geq d^n$. This shows that c_n grows exponentially in n.