

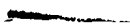
RENORMALIZATION GROUP THEORY OF MACROMOLECULES

Karl F. Freed

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PREFACE

This book is based on courses in advanced statistical mechanics given in Chicago in 1969 and 1982. A draft of the first nine chapters was used for a series of lectures at the University of Minnesota at Minneapolis in 1984. I am grateful to the participants of these courses for their comments, verbal and otherwise, which have helped in the writing of the book.

A special note of gratitude goes to Sam Edwards, who introduced me to the subject of the statistical mechanics of polymers while I was a postdoc at Manchester. The work upon which the book is based arises from the research done with my students, postdocs, and visiting scholars, R. S. Adler, M. G. Bawendi, B. J. Cherayil, J. F. Douglas, H. P. Gillis, A. L. Kholodenko, M. K. Kosmos, A. Miyake, M. Muthukumar, A. M. Nemirovsky, Y. Oono (and his collaborator T. Ohta), and S. Q. Wang, who have worked on various aspects of polymer excluded volume and without whom this book would not have been possible. A special note of thanks goes to Y. Oono for introducing me to the direct renormalization group methods. Some of the research was done concurrent with the writing of the book. Several subjects are not discussed because of my interest in providing only an introduction to both renormalization group methods and their application to polymers. Some of these further subjects are briefly described in Chapter 14 to direct the interested reader to the original references which should be accessible after reading this book.

A number of people have made detailed comments on portions of the manuscript and these include Sam Edwards, Peter Harrowell, and Arkady Kholodenko. In addition, Mounji Bawendi, Binny Cherayil, Jack Douglas, and Adolfo Nemirovsky have gone through several versions of the manuscript and have provided critical comments and suggestions for improvement. They have all eased a difficult task.

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*Chicago, Illinois
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1

INTRODUCTION

The theoretical description of the static and dynamic properties of polymers in solution, the melt, or the solid state is both fundamentally important and enormously complicated. Attempts to formulate a general theory of the physics of polymers have until recently been beset by severe mathematical difficulties, in part because the intramolecular and intermolecular polymer-polymer interactions lead to the presence of long-range correlations in polymer systems. These complexities have stimulated the use of Monte Carlo simulations of polymers which have furthered our understanding of these interesting systems. Recently, however, new theoretical methods have been developed for describing the properties of systems with long-range correlations; these approaches now enable a wide variety of polymer properties to be calculated in an approximate analytical form. In many instances this theory is in good agreement with experiment, and there is a growing indication that these methods will provide the desired comprehensive theory of a number of interesting polymer systems.

This book describes one of the most successful and far-reaching of these new theoretical methods, the renormalization group, and shows how it applies to the study of polymers. Emphasis is placed both on the theoretical development and on comparisons with experiment. To present the subject to an audience having possibly little or no prior exposure to the field of polymers or to renormalization group concepts, we begin this chapter with a brief description of what a polymer is, what microscopic structural aspects of polymers lead to their apparent complexity, what universal features of large length scale polymer properties provide essential simplifications in their theoretical description, and what connections exist between theories of polymers, theories of critical phenomena, and other areas of physics.

2 INTRODUCTION

A. THE PRIMARY STRUCTURE OF POLYMERS

A polymer consists of a set of sequentially bonded monomer units. When the number of bonds becomes large, the overall polymer dimensions greatly exceed those of the constituent monomers. Because of its large dimension, the polymer is also called a macromolecule. The simplest type of polymer is a sequential linear chain of monomers. For example, consider a polymer with the full carbon atom backbone of monomer units $-\text{CR}_1\text{R}_2-\text{CR}_3\text{R}_4-$, where the R_i are small pendent side groups, such as H , CH_3 , C_6H_5 , etc. This linear polymer may be schematically represented in terms of its chemical formula as



where n is the polymerization index. The simplest example of (1.1) is polyethylene, where all the R_i are hydrogen atoms. A wide variety of different polymers, each with its own unique properties, is obtained by varying the R_i and possibly the backbone chain atoms. More complicated branched structures are possible when some monomers are bonded to more than two other monomers. [The simple representation in (1.1) no longer applies in that case.] Polymers having identical repeating monomer units are called homopolymers, whereas those formed from more than one monomer type are copolymers. Monomers in copolymers may be arranged in a random sequence, in an alternating sequence, or they may be grouped in blocks. Small changes in the monomers, their arrangement along the chain, or in the branching structure can lead to profound changes in the spatial shape and distribution of the polymer and thereby greatly affect its macroscopic properties. This enormous diversity of polymer properties is reflected in their central importance technologically and in all biological systems.

Experiments on real polymer systems cannot, in general, be performed upon a single isolated chain. Thus, even if the polymer concentration is sufficiently low that chains are isolated from one another, all measurements involve contributions from a large number of different polymers in a wide variety of conformations. The measurement process, therefore, involves an average over a large ensemble of polymer molecules in identical environments, a situation making the description of polymer systems amenable to the methods of statistical mechanics.

B. LARGE-SCALE CHARACTERISTICS AND UNIVERSALITY

Another major feature of the primary structure of polymers involves the fact that the bond lengths, for example, the equilibrium lengths of the C—C bonds in (1.1), and the angles between successive C—C bonds are fixed. While such short-scale geometric characteristics might be thought to complicate the description of the polymer, they are actually rather unimportant when considering the properties of polymers on length scales much large than the size of a single monomer. Just as the naked eye cannot resolve individual atoms, so also an instrument measuring on length scales on the order of entire polymer dimensions cannot resolve the intricate structure of the individual monomers, and only the universal chainlike nature of the polymer is perceptible.

We cite the following as examples of the insensitivity of long wavelength polymer properties to the intricate details of monomer structure: At the most basic level, if M_A is the monomer molecular weight in a homopolymer with polymerization index n , then the total molecular weight M of the polymer is nM_A and is clearly independent of both monomer geometry and branching structure. Likewise, the radius of gyration R_G of a polymer, an experimentally measurable quantity related to the distribution of monomers about the center of mass, provides an average measure of the size of the macromolecule without detailed reference to the underlying fine structure. A commonly studied polymer-solvent system is polystyrene in cyclohexane, where polystyrene of molecular weights up to 4×10^7 is available. The individual styrene monomer molecular weight is 104, providing an idea of the number of monomers in the molecule. The radius of gyration in Angstrom units is found to be given by

$$R_G \simeq 0.3(M)^{1/2}$$

so readily accessible chains with $M = 10^6$ have $R_G \simeq 300 \text{ \AA}$.

Other commonly measured polymer properties also reflect the polymer size and not the detailed organization of individual monomers. The hydrodynamic radius R_H describes the apparent "hydrodynamic" size of a polymer as it drifts through a fluid; the second osmotic virial coefficient A_2 is proportional to an effective volume excluded to a polymer by another polymer in solution; and the intrinsic viscosity $[\eta]$ is another measure of the polymer's hydrodynamic volume influencing the rate of energy dissipation in shear flow of the polymer solution. All of these gross measures of polymer dimensions are found [1-3] under many conditions to vary as a power law of M ,

$$P = KM^a \quad (P = R_G, R_H, A_2 \text{ or } [\eta]) \quad (1.2)$$

where the prefactor K and exponent a generally depend on the property, polymer, solvent, and temperature, as well as being slowly varying functions of molecular weight M itself [1-8].

A combination of experimental data, the results of various theories discussed in Chapter 4 [1, 2] and computer simulation data [9-15] suggest that equilibrium polymer properties such as R_G and A_2 can be described by universal functions of a single phenomenological parameter [1, 16] z that is proportional to $M^{1/2}$ and to $1 - (\theta/T)$, where T is the absolute temperature and θ is called the theta temperature [1] at which $A_2 = 0$ for a particular polymer-solvent system. Hence, we anticipate universality for long wavelength equilibrium polymer properties to be expressed in the form of universal functions of z . Furthermore, the only system dependence is expected to occur in the parameter θ and in the proportionality factor between z and $M^{1/2}[1 - (\theta/T)]$, parameters that are complicated many-body functions of the microscopic details of the polymer structure and the polymer-polymer and polymer-solvent interactions and that we make no attempt here to evaluate from theory [16]. Instead, these few system-dependent parameters are determined by comparison with experimental data [17].

The simplifications introduced by considering long wavelength polymer properties have their counterparts in many other areas of physics where very different systems may be characterized by universal long wavelength descriptions in which the only reference to the particular material enters through a few system-dependent phenomenological parameters. Examples include sound propagation through solids and the hydrodynamics of fluids. Analogies with the latter can be used to understand the universal laws governing large-scale polymer properties. Molecular fluids have rather complicated dynamics emerging from the intricate molecular structure of their components and from the interactions between them. Nevertheless, on length scales very large compared to the size of an individual molecule and on time scales very long compared to characteristic molecular times, it is possible to derive [18] general hydrodynamic equations for any molecular fluid where the dependence on the particular constituent molecules enters only through a few specific parameters such as mass density, shear and bulk viscosities, heat capacity, etc. The latter quantities are extremely difficult to evaluate from first principles, and no satisfactory dynamical theory currently exists for their computation, except in the limit of rather low densities [19]. Nevertheless, the important lesson for our study of long wavelength polymer properties is the fact that many-body, collective characteristics of a fluid may be summarized by a set of universal hydrodynamic equations.

In order to succeed in deriving long wavelength universal laws for polymers, some guidance is needed in the selection of a suitable model. Again, the analogy with the universal nature of hydrodynamics offers some insight.

Consider the extreme example of a fluid composed of elephants that obey the laws of classical mechanics and that interact through elephant–elephant potentials. Such a model, radical as it is, produces long wavelength hydrodynamic equations *identical* to those of a model with realistic intermolecular interactions; the only difference between the two treatments occurs in certain parameters that are generally treated only empirically. In the same way we anticipate that the desired long wavelength universal polymer laws are derivable from models of varying levels of complexity and faithfulness to the actual microscopic details of the polymer structure and interactions.

C. A MINIMAL MODEL

The first step in developing theories of large length scale polymer properties involves the introduction of a minimal model that adequately describes all these polymer properties using the smallest possible number of phenomenological parameters. One of the simplest models of this kind views the polymer as a random walk [20–24] of sequences of uncorrelated steps corresponding to the spatial placement of the monomer units. This random-walk polymer model successfully describes homopolymers under “ideal” or theta conditions where A_2 vanishes. As described in Chapter 2, the models adequately explain the empirical finding that R_G , R_H , and $[\eta]$ are all proportional to $M^{1/2}$ at the theta point.

Away from the theta point, A_2 no longer vanishes, and the power-law exponents a for R_G , R_H , and $[\eta]$ no longer equal $\frac{1}{2}$ [3]. A more sophisticated model with other features is therefore needed for these more general situations. As discussed more fully in subsequent chapters, this additional feature involves inclusion of interactions between the constituent monomers on the polymer (the polymer–polymer interactions), leading to popular models of polymers as self-interacting random walks [2, 9–15, 25, 26].

D. SHORT-RANGE CORRELATIONS AND FLEXIBILITY IN POLYMERS

Somewhat more realistic models of polymers [1, 2, 4, 27, 28] under theta conditions incorporate some degree of freedom of rotation about the single bonds joining the monomers. For instance, let ϕ specify the angle of rotation (say between R_1 and R_3) about a particular C–C bond in (1.1). Then many polymers have a potential energy [4] $V(\phi)$ arising from interactions between the R_i groups on the two bonded carbon atoms (and also between the

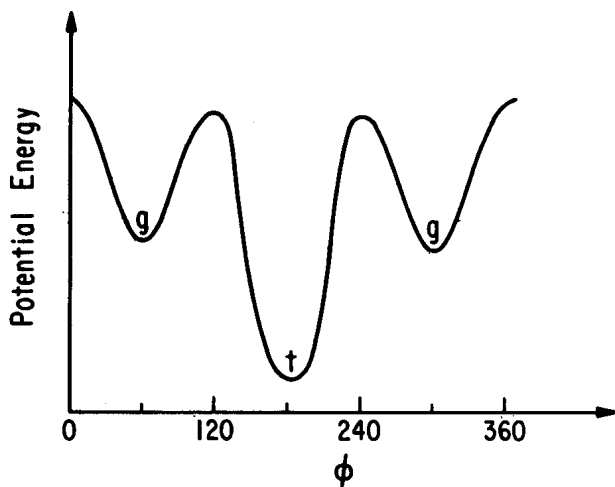


Figure 1.1. A schematic representation of the hindered rotational potential $V(\phi)$ as a function of rotation angle ϕ about C-C single bonds. The minima correspond to the trans state t and the gauche state g .

neighboring bonded monomers) which is of the general form displayed in Fig. 1.1, having three minima at the preferred orientations of the R_i groups (and the bonds to adjacent monomers) on the two bonded carbon atoms. Models such as this one and others in which there are correlations between the angles ϕ for neighboring bonds can be shown to be related to Markov processes (see Chapter 2, Section 2-D-3) or to one-dimensional Ising models. As a result they are amenable to exact solution [6].

A more subtle type of model contains repulsive interactions between nonbonded monomers when the monomers approach each other closely enough in space. The short-range interactions must be repulsive because two different monomers cannot occupy the same region of space. These "excluded volume" interactions introduce couplings between the degrees of freedom ϕ_i for each of the monomers, leading to a many-body problem that cannot be solved in closed form. A typical excluded volume interaction is depicted schematically in Fig. 1.2 for a continuous chain model of a polymer. The two interacting monomers are distant from each other along the chain but close in space. The freedom of rotation about the bonds near these monomers can result in short-range repulsive encounters between nearby monomers. In this way excluded volume interactions couple the rotational degrees of freedom ϕ_i of different monomers. Because these excluded volume interactions can, in principle, occur between all pairs of monomers, separated by a sufficient distance along the chain, the polymer excluded volume problem is evidently a

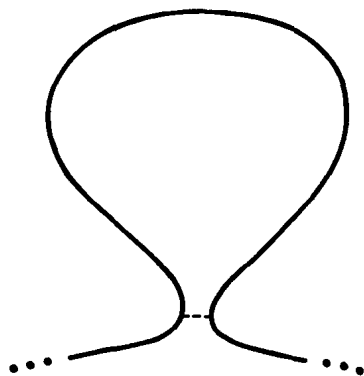


Figure 1.2. Schematic representation of an excluded volume interaction for a continuous polymer chain. Dotted lines designate segments close enough to interact.

many-body problem, and its intractability is compounded by chain connectivity and short-range correlations [2, 25, 26]. Neither effect appears in the treatment of excluded volume in small molecules [19].

E. STATISTICAL MECHANICS OF POLYMER INTERACTIONS AND COARSE GRAINING

As noted earlier, our primary interest in this book is in flexible polymers having some degree of freedom of rotation about the single bonds joining the monomers. A single long polymer chain of this type possesses an enormous number of different conformations (or polymer configurations). Given the potentials describing hindered (or free) rotation about the single bonds, the steric interactions between nearby bonds and the excluded volume interaction, it follows from the general principles of statistical mechanics that the (unnormalized) probability density of finding a particular chain conformation is given by the Boltzmann factor $\exp(-\beta V)$ where $\beta = 1/k_B T$, k_B is Boltzmann's constant, and V is the total potential energy evaluated for that chain configuration. Thermodynamic properties of the polymer system and the normalization factor for the chain-conformation probability density are obtained from averages over all possible chain conformations with the weight $\exp(-\beta V)$. This averaging is over all possible polymer degrees of freedom for either a single polymer chain or for a collection of polymers at nonzero concentrations. Because of the large number of degrees of freedom available to the polymers, it will be appreciated that even the simplest, realistic models of the long wavelength properties of polymers pose highly complicated mathematical problems made worse by the presence of excluded volume.