

Scaling Concepts in Polymer Physics

by the same author

The Physics of Liquid Crystals

Superconductivity of Metals and Alloys

Scaling Concepts in Polymer Physics

Pierre-Gilles de Gennes

CORNELL UNIVERSITY PRESS

Ithaca and London

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First published 1979 by Cornell University Press.

Published in the United Kingdom by Cornell University Press Ltd.,
2-4 Brook Street, London W1Y 1AA.

International Standard Book Number 0-8014-1203-X

Library of Congress Catalog Card Number 78-21314

Printed in the United States of America

Librarians: Library of Congress cataloging information appears on the last page of the book.

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Who hath measured the waters in the hollow of
his hand, and weighed the mountains in scales?
ISAIAH 40, 12

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1.

Preface

The physics of long flexible chains was pioneered by several great scientists: Debye, Kuhn, Kramers, Flory, and so forth. They constructed the basic ideas; those concerning static properties are summarized in Flory's book,¹ and those concerning dynamics in various reviews.^{2,3,4} More recently, a second stage in the physics of polymers has evolved, because of the availability of new experimental and theoretical tools. As usual, these new techniques brought about some important changes in our viewpoints.

(i) *Neutron diffraction* allowed for measurements of polymer conformations at large scales which were not feasible with X-rays. The essential point is that different isotopes give different scattering amplitudes for neutrons.⁵ Thus, it became possible to label one chain (replacing, for instance, its protons by deuterons) and to observe it individually in a sea of chemically identical but unlabeled chains. The same operation is not feasible with X-rays, for which the labeling is based on the attachment of heavy atoms to the chain; these atoms make the labeled and unlabeled species very different, and spurious segregation effects always occur. The advent of neutron scattering experiments on labeled species opened up a vast new field; precise data on long-range conformations and correlations became available rapidly.

(ii) *Light scattering* has traditionally been used for measurements of molecular weights and sizes in dilute solution. This technique, however, was limited and delicate, mainly because of the many spurious sources of scattering (e.g., dust) which were always present. The situation suddenly improved when the *inelastic* scattering of laser light became accessible.

This "photon beat" method⁶ allows one to study the dynamics of the scattering centers in a frequency range (1 to 10^6 cycles) which is suitable for the overall motions of polymer chains. Furthermore, all the spurious signals caused by dust particles are easier to eliminate, since large particles are essentially immobile and contribute only to the elastic spectrum.

(iii) A certain refinement also occurred in *theoretical methods*. Functional integrals, Feynman diagrams, and all the techniques of many-body theory were first applied to polymers in the pioneering work of S. F. Edwards.⁷ In a different direction, certain *numerical methods*, allowing the study of polymer statistics on simple lattice models, became extremely powerful. The British school used exact summation on short chains, supplemented by clever extrapolation techniques to reproduce the behavior of long chains.⁸ Another approach (with a slightly different spectrum of application) was the Monte Carlo method, in which a small (but representative) fraction of all possible conformations in a given problem is generated and sampled.⁹ Both techniques have been extremely helpful in elucidating certain geometric laws and in displaying the existence of "characteristic exponents," to which we constantly refer in this book.

In a third stage, a relationship between polymer statistics and phase transition problems was discovered.^{10,11} This discovery allowed polymer science to benefit from the vast knowledge which had been accumulated on critical phenomena; a number of remarkably simple *scaling* properties emerged. At this third stage, however, our community is divided; a new theoretical language (heavily loaded with field theoretical concepts) has appeared but has remained essentially unintelligible to most polymer scientists.

The aim of this book is to eliminate this barrier, or at least to reduce it as much as possible. In a series of lectures given between 1975 and 1978, in Paris, Strasbourg, Grenoble, and Leiden, I found that most of the essential concepts of polymer physics can be explained in simple terms and do not require any advanced theoretical education. Thus, I hope to give to my reader a reasonable understanding of certain "universal" properties: scaling laws and characteristic exponents in polymer solutions and melts. All details are systematically omitted.

(i) I ignore numerical coefficients in most formulas, where they would obscure the main line of thought.

(ii) On the experimental side, the discussions are very brief. I do not try to recapitulate all the data on a given problem but simply to select studies in which scaling features are apparent.

(iii) On the other hand, this book is not intended as an introduction for

a young polymer theorist. Theoretical methods are relegated to the last three chapters; and even there my aim is not to provide the reader with the ability to make advanced calculations; more modestly, I would like him (or her) to reach a certain qualitative understanding of the methods—how they work and where they fail. (A much more complete description of polymer theory will be available in a forthcoming book by J. des Cloiseaux and G. Jannink.)

(iv) Certain important areas of polymer physics are not mentioned at all; crystallization kinetics and glass transitions are two glaring examples. Polyelectrolytes are mentioned only briefly. In these areas we do not know whether or not scaling concepts will be really useful.

On the whole, this book is meant for experimentalists in polymer science who wish to incorporate the recent advances into their modes of thinking. Obviously certain difficulties remain even for these readers. In particular there is a general question of language and notation.

(i) I have tried to follow the basic notation of Flory,¹ but I have had to introduce some modifications which correspond to recent trends—for instance, to use a polymerization index (N) rather than a molecular weight (M) as the fundamental object; to eliminate all mention of Avogadro's number; to write thermal energies as T rather than $k_B T$ (i.e., to use energy units for the temperature T , as is done now in most theoretical literature); and so forth. Such modifications, although trivial, will disturb the reader at the beginning, but they represent (I think) a necessary simplification.

(ii) At a more fundamental level, my inclination is always to seek comparisons to other branches of science: conceptually, a single chain in an external field is closely related to a quantum particle, as first found by Edwards; there is a profound analogy between polymer statistics and phase transitions; the gelation problem is related to the general concept of percolation; and so forth. I have tried to explain some of these analogies, without assuming prior knowledge of quantum mechanics or critical phenomena (a summary of critical phenomena is included in Chapter X). One pleasant discovery, when I was teaching polymer statistics, was to find that renormalization groups can be explained in very simple words to polymer chemists; the last chapter describes this approach.

I have also tried to help my readers by carefully selecting references. As explained, I never give a complete historical list on any topic; I quote mainly a few basic reviews which are both clear and accessible. (Most of the polymer literature written before 1965 and relevant to the present text is analyzed in the books mentioned at the beginning of this preface.) For the more recent advances on scaling laws, the majority of my references are French. This is not an expression of nationalistic pride; it

just happened that our experimentalists, under the impetus of H. Benoît in Strasbourg and G. Jannink in Saclay, were able to set up at the right time an efficient, cooperative effort for elucidating scaling laws. The present text reflects to a large extent the discussions of this program during the past five or six years.

The laboratories at Strasbourg, Saclay, and Collège de France that joined in this venture have been associated for some time under the acronym STRASACOL, the story of which is summarized in a short note.¹² However, the cooperation has rapidly extended beyond these limits, involving people at Brest, Grenoble, and Chambéry, and I hope it expands even further. To all these units I am profoundly grateful, for their eagerness in discussing present research and for their open mind toward new directions. Last but not least, I wish to mention my debt to many friends on the theoretical side: to C. Sadron; to J. des Cloiseaux, G. Sarma, and M. Daoud in Saclay; to F. Brochard and P. Pfeuty in Orsay; to S. F. Edwards in England; and especially to our foreign visitors: S. Alexander, J. Ferry, F. C. Frank, P. Martin, P. Pincus, and W. Stockmayer, who instructed us and corrected many of my mistakes.

Some mistakes certainly remain, and at various points I present very conjectural views. Nevertheless, let us hope that the book will still give a reasonable image of what is universal and what is system dependent in these fascinating systems of mobile entangled chains.

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