

# **Scaling Concepts in Polymer Physics**

**高分子物理学中的标度概念**

**Pierre-Gilles de Gennes**

Cornell University Press  
世界图书出版公司

# Scaling Concepts in Polymer Physics

Pierre-Gilles de Gennes

CORNELL UNIVERSITY PRESS  
*Ithaca and London*

书 名: Scaling Concepts in Polymer Physics  
作 者: Pierre-Gilles de Gennes  
中 译 名: 高分子物理学中的标度概念  
出 版 者: 世界图书出版公司北京公司  
印 刷 者: 北京世图印刷厂  
发 行: 世界图书出版公司北京公司 (北京朝内大街 137 号 100010)  
联系电话: 010-64015659, 64038347  
电子信箱: kjsk@vip.sina.com  
开 本: 大 32 印 张: 10.5  
出版年代: 2003 年 6 月  
书 号: 7-5062-6000-X/O · 389  
版权登记: 图字: 01-2003-3131  
定 价: 45.00 元

世界图书出版公司北京公司已获得 Cornell University Press 授权在中国大陆独家重印发行。

# Contents

Preface 13

Introduction: Long Flexible Chains 19

## Part A

### STATIC CONFORMATIONS

A Single Chain 29

I.1.	The Notion of an Ideal Chain	29
I.1.1.	Simple random walks	29
I.1.2.	More general models for ideal chains	31
I.1.3.	Ideal chains under external actions	33
I.1.4.	Pair correlations inside an ideal chain	36
I.1.5.	Summary	38
I.2.	A "Real" Chain in a Good Solvent	38
I.2.1.	The main experiments	38
I.2.2.	Numerical data on self-avoiding walks	39
I.2.3.	Correlations inside a swollen coil	42
I.2.4.	Summary	43
I.3.	The Flory Calculation of the Exponent $\nu$	43
I.3.1.	Principles	43
I.3.2.	Chains are ideal above four dimensions	45

I.3.3. Why is the Flory method successful?	46
<b>I.4. Constrained Chains</b>	<b>46</b>
I.4.1. A chain under traction	47
I.4.2. Squeezing a real chain in a tube	49
<b>Polymer Melts</b>	<b>54</b>
 II.1. Molten Chains Are Ideal	54
II.1.1. A self-consistent field argument	54
II.1.2. Screening in dense polymer systems	56
II.1.3. One long chain among shorter chains	59
II.1.4. Mixed chains versus segregated chains	60
II.1.5. Summary	61
<b>II.2. Microscopic Studies of Correlations in Melts</b>	<b>62</b>
II.2.1. Necessity of labeled species	62
II.2.2. The correlation hole	62
II.2.3. More general sequences	64
II.2.4. The correlation hole in two dimensions	66
II.2.5. Mixtures of labeled and unlabeled chains	66
II.2.6. Summary	67
<b>Polymer Solutions in Good Solvents</b>	<b>69</b>
 III.1. The Mean Field Picture (Flory-Huggins)	69
III.1.1. Entropy and energy in a lattice model	69
III.1.2. Low concentrations	73
III.1.3. Osmotic pressures	74
III.1.4. Critique of mean field theory	76
<b>III.2. Scaling Laws for Athermal Solvents</b>	<b>76</b>
III.2.1. The overlap threshold $c^*$	76
III.2.2. The dilute regime	77
III.2.3. Semi-dilute solutions	78
III.2.4. The correlation length	80
III.2.5. The notion of blobs	81
III.2.6. Correlation functions	82
III.2.7. Screening in semi-dilute solutions	85
<b>III.3. Confined Polymer Solutions</b>	<b>88</b>
III.3.1. A semi-dilute solution in contact with a repulsive wall	88
III.3.2. A semi-dilute solution in a cylindrical pore	91

## IV

Incompatibility and Segregation	98
IV.1. General Principles and Questions	98
IV.1.1. The trend toward segregation	98
IV.1.2. Cases of partial compatibility	99
IV.1.3. Specific features of polymer segregation	102
IV.2. Polymer-Polymer Systems	103
IV.2.1. Thermodynamic Principles	103
IV.2.2. The coexistence curve in the symmetrical case	105
IV.2.3. Metastable states and the spinodal curve	107
IV.2.4. The critical point	107
IV.2.5. Critical fluctuations	108
IV.2.6. Absence of anomalous exponents	112
IV.3. Polymer Plus Poor Solvent	113
IV.3.1. Regions in the phase diagram	113
IV.3.2. A single coil near $T = \Theta$	115
IV.3.3. Semi-dilute solutions at $T = \Theta$	117
IV.3.4. Semi-dilute solutions: crossover between good and poor solvent	119
IV.3.5. Vicinity of the coexistence curve	121
IV.4. Polymer Plus Polymer Plus Solvent	123
IV.4.1. Good solvent and strong segregation factor	124
IV.4.2. Good solvent and weak segregation factor	125
IV.4.3. Theta solvents	126

## V

Polymer Gels	128
V.1. Preparation of Gels	128
V.1.1. Chemical pathways	129
V.1.2. Unorthodox gelation processes	130
V.1.3. Physical gelation	133
V.1.4. Strong gelation versus weak gelation	134
V.1.5. Relationship between preparation and properties of gels	135
V.2. The Sol-Gel Transition	137
V.2.1. The classical picture	137
V.2.2. Gelation without solvent: the percolation model	137
V.2.3. Large clusters below the gelation threshold	138
V.2.4. Gel properties just above threshold	140
V.2.5. A quick glance at the classical theory	142
V.2.6. The classical theory works in six dimensions	145

V.2.7.	The special case of vulcanization	146
V.2.8.	Dilution effects: competition between gelation and precipitation	148
V.3.	Gels in Good Solvents	152
V.3.1.	The $c^*$ theorem	152
V.3.2.	Pair correlations in the gel	153
V.3.3.	Elasticity of swollen gels	156
V.3.4.	Spinodal decomposition	158
V.3.5.	Summary	160

## Part B

### DYNAMICS

## VI

### Dynamics of a Single Chain

165

VI.1.	Historical Background	165
VI.1.1.	The Rouse model	165
VI.1.2.	Weakness of internal friction effects	167
VI.1.3.	Critique of the mode concept	171
VI.2.	Dynamic Scaling in Good Solvents	173
VI.2.1.	The Kirkwood approximation for chain mobility	173
VI.2.2.	Inelastic scattering of light	177
VI.2.3.	The fundamental relaxation time	179
VI.2.4.	Static viscosity of dilute solutions	182
VI.2.5.	Frequency dependence of viscosities	185
VI.3.	Special Flow Problems	186
VI.3.1.	Deformation in strong extensional flows	186
VI.3.2.	Dynamics of a chain inside a cylindrical pore	193
VI.4.	Problems of Internal Friction	198
VI.4.1.	Three forms of friction	198
VI.4.2.	Evidence for the Cerf term	199
VI.4.3.	Origin of the Cerf friction	200
VI.4.4.	Summary	203

## VII

### Many-Chain Systems: The Respiration Modes

205

VII.1.	Semi-Dilute Solutions	205
VII.1.1.	Longitudinal modes	205
VII.1.2.	Two diffusion coefficients	208

VII.1.3.	The sedimentation coefficient	208
VII.1.5.	Cooperative diffusion	210
VII.1.5.	Summary	211
VII.2.	Dynamics near a Critical Point	212
VII.3.	Dynamics of Gels	214
VII.3.1.	Longitudinal modes of swollen gels	214
VII.3.2.	Slow motions near the spinodal threshold	215
VII.3.3	Dynamics at the sol-gel transition	216

**VIII****Entanglement Effects**      219

VIII.1.	Dynamics of Melts and Concentrated Solutions	219
VIII.1.1.	Rubber-like and liquid-like behaviors	219
VIII.1.2.	Elastic modulus of the transient network	221
VIII.1.3.	Viscosity and terminal time	222
VIII.2.	Reptation of a Single Chain	223
VIII.2.1.	Coils trapped in a network	223
VIII.2.2.	The terminal time, $\tau_t$	224
VIII.2.3.	Translational diffusion	227
VIII.2.4.	Reptation in swollen systems	227
VIII.2.5.	Reptation of a branched chain	230
VIII.3.	Conjectures on Polymer Melts	234
VIII.3.1.	One long chain in a melt of shorter chains	234
VIII.3.2.	Newtonian viscosities in a homodisperse melt	236
VIII.3.3.	Behavior in strong transverse shear flows	237
VIII.3.4.	Critical dynamics in entangled binary mixtures	238
VIII.3.5.	Summary	240

**Part C****CALCULATION METHODS****IX****Self-Consistent Fields and Random Phase Approximation**      245

IX.1.	General Program	245
IX.2.	Self-Consistent Fields	246
IX.2.1.	An ideal chain under external potentials	246
IX.2.2.	Situations of ground state dominance	250
IX.2.3.	Self-consistency with ground state dominance	254
IX.3.	The Random Phase Approximation for Dense Chains	258

IX.3.1.	Definition of response functions	259
IX.3.2.	Response functions for noninteracting chains	260
IX.3.3.	Self-consistent calculation of responses	262

**X****Relationships between Polymer Statistics  
and Critical Phenomena** 265

X.1.	<b>Basic Features of Critical Points</b>	265
X.1.1.	Large correlated regions	265
X.1.2.	Critical exponents for a ferromagnet	267
X.1.3.	Relations among exponents	268
X.1.4.	Correlation functions	269
X.1.5.	The $n$ vector model	271
X.2.	<b>The Single Chain Problem</b>	272
X.2.1.	The limit $n = 0$	272
X.2.2.	The magnetic partition function expanded in self-avoiding loops	275
X.2.3.	Spin correlations and the one-chain problem	276
X.2.4.	Properties of self-avoiding walks	277
X.3.	<b>Many Chains in a Good Solvent</b>	281
X.3.1.	The des Cloiseaux trick	281
X.3.2.	Overlap concentration $\Phi^*$ and related scaling laws	284
X.3.3.	Crossover between dilute and semi-dilute solutions	285
X.3.4.	Correlations in the solution	286
X.3.5.	Current extensions	286
X.3.6.	What is the order parameter?	287

**XI****An Introduction to Renormalization Group Ideas** 290

XI.1.	<b>Decimation along the Chemical Sequence</b>	290
XI.1.1.	A single chain in a good solvent	290
XI.1.2.	Grouping the monomers into subunits	291
XI.1.3.	Iterating the process	293
XI.1.4.	Existence of a fixed point	293
XI.1.5.	Scaling law for the chain size	294
XI.1.6.	Free energy of a single chain	295
XI.1.7.	Calculations near four dimensions	298
XI.2.	<b>Applications</b>	299
XI.2.1.	Polyelectrolytes	299

XI.2.2. Collapse of a single chain	304
XI.2.3. Semi-dilute solutions and blobs	313
Author Index	317
Subject Index	321

# 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*

Copyright © 1979 by Cornell University

All rights reserved. Except for brief quotations in a review, this book, or parts thereof, must not be reproduced in any form without permission in writing from the publisher. For information, address Cornell University Press, Sage House, 512 East State Street, Ithaca, New York 14850.

First published 1979 by Cornell University Press

Printed in the United States of America

LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA  
(For library cataloging purposes only)

Gennes, Pierre G de.

Scaling concepts in polymer physics.

Includes bibliographical references and indexes.

1. Polymers and polymerization. I. Title.

QD381.G45 547'.84

78-21314

International Standard Book Number 0-8014-1203-X

Library of Congress Catalog Card Number 78-21314

Cornell University Press strives to use environmentally responsible suppliers and materials to the fullest extent possible in the publishing of its books. Such materials include vegetable-based, low-VOC inks and acid-free papers that are recycled, totally chlorine-free, or partly composed of nonwood fibers. Books that bear the logo of the FSC (Forest Stewardship Council) use paper taken from forests that have been inspected and certified as meeting the highest standards for environmental and social responsibility. For further information, visit our website at [www.cornellpress.cornell.edu](http://www.cornellpress.cornell.edu).

This reprint edition is specially licensed by the original publisher,  
Cornell University Press, for sale in China only.

# Contents

Preface 13

Introduction: Long Flexible Chains 19

## Part A

### STATIC CONFORMATIONS

A Single Chain 29

I.1.	The Notion of an Ideal Chain	29
I.1.1.	Simple random walks	29
I.1.2.	More general models for ideal chains	31
I.1.3.	Ideal chains under external actions	33
I.1.4.	Pair correlations inside an ideal chain	36
I.1.5.	Summary	38
I.2.	A "Real" Chain in a Good Solvent	38
I.2.1.	The main experiments	38
I.2.2.	Numerical data on self-avoiding walks	39
I.2.3.	Correlations inside a swollen coil	42
I.2.4.	Summary	43
I.3.	The Flory Calculation of the Exponent $\nu$	43
I.3.1.	Principles	43
I.3.2.	Chains are ideal above four dimensions	45

I.3.3. Why is the Flory method successful?	46
<b>I.4. Constrained Chains</b>	<b>46</b>
I.4.1. A chain under traction	47
I.4.2. Squeezing a real chain in a tube	49
<b>Polymer Melts</b>	<b>54</b>
 II.1. Molten Chains Are Ideal	54
II.1.1. A self-consistent field argument	54
II.1.2. Screening in dense polymer systems	56
II.1.3. One long chain among shorter chains	59
II.1.4. Mixed chains versus segregated chains	60
II.1.5. Summary	61
<b>II.2. Microscopic Studies of Correlations in Melts</b>	<b>62</b>
II.2.1. Necessity of labeled species	62
II.2.2. The correlation hole	62
II.2.3. More general sequences	64
II.2.4. The correlation hole in two dimensions	66
II.2.5. Mixtures of labeled and unlabeled chains	66
II.2.6. Summary	67
<b>Polymer Solutions in Good Solvents</b>	<b>69</b>
 III.1. The Mean Field Picture (Flory-Huggins)	69
III.1.1. Entropy and energy in a lattice model	69
III.1.2. Low concentrations	73
III.1.3. Osmotic pressures	74
III.1.4. Critique of mean field theory	76
<b>III.2. Scaling Laws for Athermal Solvents</b>	<b>76</b>
III.2.1. The overlap threshold $c^*$	76
III.2.2. The dilute regime	77
III.2.3. Semi-dilute solutions	78
III.2.4. The correlation length	80
III.2.5. The notion of blobs	81
III.2.6. Correlation functions	82
III.2.7. Screening in semi-dilute solutions	85
<b>III.3. Confined Polymer Solutions</b>	<b>88</b>
III.3.1. A semi-dilute solution in contact with a repulsive wall	88
III.3.2. A semi-dilute solution in a cylindrical pore	91

## IV

## Incompatibility and Segregation 98

IV.1.	General Principles and Questions	98
IV.1.1.	The trend toward segregation	98
IV.1.2.	Cases of partial compatibility	99
IV.1.3.	Specific features of polymer segregation	102
IV.2.	Polymer-Polymer Systems	103
IV.2.1.	Thermodynamic Principles	103
IV.2.2.	The coexistence curve in the symmetrical case	105
IV.2.3.	Metastable states and the spinodal curve	107
IV.2.4.	The critical point	107
IV.2.5.	Critical fluctuations	108
IV.2.6.	Absence of anomalous exponents	112
IV.3.	Polymer Plus Poor Solvent	113
IV.3.1.	Regions in the phase diagram	113
IV.3.2.	A single coil near $T = \Theta$	115
IV.3.3.	Semi-dilute solutions at $T = \Theta$	117
IV.3.4.	Semi-dilute solutions: crossover between good and poor solvent	119
IV.3.5.	Vicinity of the coexistence curve	121
IV.4.	Polymer Plus Polymer Plus Solvent	123
IV.4.1.	Good solvent and strong segregation factor	124
IV.4.2.	Good solvent and weak segregation factor	125
IV.4.3.	Theta solvents	126

## V

## Polymer Gels 128

V.1.	Preparation of Gels	128
V.1.1.	Chemical pathways	129
V.1.2.	Unorthodox gelation processes	130
V.1.3.	Physical gelation	133
V.1.4.	Strong gelation versus weak gelation	134
V.1.5.	Relationship between preparation and properties of gels	135
V.2.	The Sol-Gel Transition	137
V.2.1.	The classical picture	137
V.2.2.	Gelation without solvent: the percolation model	137
V.2.3.	Large clusters below the gelation threshold	138
V.2.4.	Gel properties just above threshold	140
V.2.5.	A quick glance at the classical theory	142
V.2.6.	The classical theory works in six dimensions	145