

Contents

<i>Preface</i>	ix
<i>Acknowledgement</i>	xii
1 Introduction	1
2 Basics about polymers	10
2.1 Gaussian chains – heuristic introduction	10
2.2 Gaussian chains – path integrals	12
2.3 Self-interacting chains	15
3 Many-chain systems: melts and screening	19
3.1 Some general remarks	19
3.2 Collective variables	20
3.3 The statistics of tagged chains	26
4 Rubber formation	31
4.1 Classical theory of gelation	31
4.2 Percolation	34
4.3 Vulcanization	37
5 The elastomer matrix	40
5.1 General remarks	40
5.2 The Gaussian network	42
5.3 Entanglements and the tube model: a material law	45
5.3.1 Entanglement sliding	47
5.3.2 Finite extensibility	49
5.3.3 Tube and sliplinks	52

5.4	Experiments	53
5.4.1	The stress–strain relationship	53
5.4.2	The extended tube model of rubber elasticity	55
5.4.3	Testing of the model	59
6	Polymers of larger connectivity: branched polymers and polymeric fractals	64
6.1	Preliminary remarks	64
6.2	<i>D</i> -dimensionally connected polymers in a good solvent	64
6.3	<i>D</i> -dimensionally connected polymers between two parallel plates in a good solvent	66
6.4	<i>D</i> -dimensionally connected polymers in a cylindrical pore (good solvent)	68
6.5	Melts of fractals in restricted geometries	71
6.6	Once more the differences	74
7	Reinforcing fillers	75
7.1	Fillers for the rubber industry	75
7.2	Carbon black	77
7.2.1	Morphology of carbon black aggregates	77
7.2.2	Surface roughness of carbon blacks	84
7.2.3	Energy distribution of carbon black surfaces	92
7.3	Silica	96
8	Hydrodynamic reinforcement of elastomers	101
8.1	Reminder: Einstein–Smallwood	101
8.2	Rigid filler aggregates with fractal structure	103
8.2.1	Effective medium theory and linear elasticity	106
8.2.2	Screening lengths	109
8.2.3	Reinforcement by fractal aggregates	110
8.3	Core–shell systems	111
8.3.1	Uniform soft sphere	112
8.3.2	Soft core/hard shell	112
8.3.3	Hard core/soft shell	115
9	Polymer–filler interactions	118
9.1	General remarks and scaling	118
9.1.1	Flat surface	119
9.1.2	Generalization for fractal surfaces	120

<i>Contents</i>	vii
9.2 Variational calculation statics	121
9.2.1 Variational calculation	121
9.3 Trial Hamiltonian	122
9.3.1 Minimization of the free energy	123
9.3.2 Effective interaction strength	126
9.4 Some further remarks on the interpretation	130
9.4.1 Modeling by random potentials	131
9.4.2 Annealed and quenched disorder	134
9.4.3 Dynamics of localized chains – freezing, glass transition at filler surfaces	135
9.5 Equation of motion for the time correlation function	137
9.5.1 Langevin dynamics	137
9.5.2 Self-consistent Hartree approximation	139
9.5.3 Equation of motion	142
9.6 Dynamic behavior of the chain	144
9.6.1 Anomalous diffusion	144
9.6.2 Center-of-mass freezing	146
9.6.3 Rouse modes freezing and a two mode toy model	147
9.7 Numerical analysis	148
9.7.1 Bifurcation diagram	149
9.8 Contribution to the modulus	151
10 Filler–filler interaction	153
10.1 Filler networking in elastomers	153
10.1.1 Flocculation of fillers during heat treatment	153
10.1.2 Kinetics of filler structures under dynamic excitation	156
10.2 Dynamic small- and medium-strain modeling – the Payne effect	161
10.2.1 The Kraus model	161
10.2.2 The viscoelastic model	164
10.2.3 The van der Walle–Tricot–Gerspacher (WTG) model	169
10.2.4 The links–nodes–blobs (LNB) model	171
10.2.5 The model of the variable network density	172
10.2.6 The cluster–cluster aggregation (CCA) model	174
10.3 Stress-softening and quasistatic stress–strain modeling – the Mullins effect	182
10.3.1 The dynamic flocculation model	182
10.3.2 The Kantor–Webman model of flexible chain aggregates	193
<i>References</i>	196
<i>Index</i>	204