

Contents

Acknowledgements	iv
Abstract	vi
Overview	1
I Reversible Gelation and Glass Transition: Towards a microscopic model of reversible polymer gel	3
1 Introduction: Gel and gelation	4
1.1 Preparation of gels	4
1.2 Gelation	5
1.3 Features of reversible gelation and relations to the glass transition	7
2 Mean field theory and the spinodal lines	11
2.1 Self-consistent field theory	12
2.1.1 Microscopic Hamiltonian of polymer mixtures	13
2.1.2 Partition function and self-consistent equations	14
2.1.2.1 Partition function	14
2.1.2.2 Self-consistent equations	15
2.2 Free energy expansion	17
2.3 Results and discussion	19
2.4 Conclusion	23
2.A Self-consistent field calculation	24
2.A.1 Calculations of the partition functions of non-interacting polymers in external fields	24
2.A.2 Grand canonical ensemble calculation	26
2.A.3 Numerical solution of the SCF equations	27
2.A.4 Analysis of the iteration scheme	28

2.B	Free Energy Expansion	30
2.B.1	Calculation of the connected correlation functions	30
2.B.2	Spinodal limit	31
3	Random isotropic structures and possible glass transitions in diblock copolymer melts	33
3.1	Introduction	33
3.2	Model and solution	36
3.2.1	Model description	36
3.2.2	Ordered states and order-disorder transition	38
3.2.3	Random structures and glass transition	41
3.3	Results and discussion	45
3.3.1	Glass transition	45
3.3.2	Glass transition vs order-disorder transition	50
3.4	Conclusions	54
3.A	Perturbative expansion of the effective potential with broken symmetries	55
3.B	Order-disorder transition	58
3.C	Approximate solution of the glass transition	59
3.D	Relationship between the pinned free energy $F[\zeta]$ and the free energy landscape of the original Hamiltonian $H[\phi]$	62
II	Interplay of Generic Interactions and Specific Binding	64
4	Thermodynamics of polymer-tethered ligand-receptor interactions between surfaces	65
4.1	Introduction	66
4.2	Model and solution	69
4.2.1	Thermodynamics of the surface interactions	69
4.2.1.1	Both-open system	72
4.2.1.2	Both-closed system	73
4.2.1.3	Open-closed system	74
4.2.2	Polymer-mediated specific interactions	75
4.2.2.1	Scaling analysis	75
4.2.2.2	Analytical calculations for the Gaussian chain	77
4.2.3	Immobile receptors and ligands: low-density limit	80
4.3	Results and discussion	81
4.3.1	Effects of the polymer tether on specific binding and non-specific interactions	83

4.3.2	Interactions between surfaces mediated by ligand-receptor binding	86
4.3.3	Composite interaction potential from specific binding and non-specific interactions	97
4.3.3.1	Cell adhesion revisited	98
4.3.3.2	Bidisperse ligand-receptor binding	100
4.3.3.3	Attempt at a synthesis	102
4.4	Conclusion	103
4.A	Polymer confined between two surfaces	105
4.A.1	Gaussian chain	105
4.A.2	Rigid rod and variants	107
4.B	Low-density expansion for the quenched problem	109
4.C	Exact results for the single-chain quenched problem	112
4.C.1	Ideal solution model	112
4.C.2	Ideal lattice gas model	113
4.D	Multi-chain quenched problem in the high-density limit	115
5	Dynamics of membrane adhesion mediated by receptor interactions	117
5.1	Introduction	118
5.2	Model and solution	120
5.2.1	Model description	120
5.2.2	Scaling analysis of the nucleation dynamics	124
5.2.3	Minimum-energy-path calculation	126
5.3	Numerical results and discussion	127
5.4	The Peierls argument near the critical unbinding transition	136
5.5	Conclusion	139
Bibliography		141