

## Contents

Foreword	v
Preface	vii
Introduction. Role of Modeling in Soft Matter Physics <i>D. Frenkel</i>	1
1. Applications of Density Functional Theory in Soft Condensed Matter <i>H. Löwen</i>	9
1 Freezing of Spheres . . . . .	11
1.1 Phenomenological results . . . . .	11
1.2 Independent treatment of the different phases . . . . .	12
1.3 Unifying Microscopic theories . . . . .	13
1.4 Phase diagrams of simple potentials . . . . .	14
1.5 Density Functional Theory (DFT) . . . . .	17
2 Brownian Dynamics . . . . .	23
2.1 Brownian dynamics (BD) . . . . .	23
2.2 BD computer simulations . . . . .	27
2.3 Dynamical density functional theory (DDFT) . . . . .	27
2.4 An example: Crystal growth at imposed nucleation clusters . . . . .	29
2.5 Hydrodynamic interactions . . . . .	31
3 Rod-Like Particles . . . . .	33
3.1 Statistical mechanics of rod-like particles . . . . .	33
3.2 Simple models . . . . .	38
3.3 Brownian dynamics of rod-like particles . . . . .	40
3.4 "Active" (self-propelled) Brownian particles . . . . .	42
4 Conclusions . . . . .	42

2.	Polymer Phase Separation	47
	<i>M. Müller</i>	
1	Introduction . . . . .	47
2	Phase Behavior in the Bulk . . . . .	56
2.1	Predictions of the mean-field theory . . . . .	56
2.2	Estimating the Flory-Huggins parameter for simulation models . . . . .	59
2.3	Simulation techniques for computing the bulk phase behavior . . . . .	63
2.4	Compressible mixtures . . . . .	70
3	Outlook: Interfacial Properties, Phase Boundaries in Confined Geometry, and Wetting . . . . .	74
3.	Self-Consistent Field Theory of Block Copolymers	85
	<i>F. Qiu, A.-C. Shi and Y. Yang</i>	
1	Introduction . . . . .	85
2	Self-Consistent Field Theory of Block Copolymers . . . . .	90
2.1	Polymer model and partition function . . . . .	90
2.2	Chain propagators . . . . .	92
2.3	Self-consistent mean-field theory . . . . .	93
3	Reciprocal-Space Formulation . . . . .	95
4	Applications of the Reciprocal-Space Method . . . . .	100
5	Summary . . . . .	101
4.	Dynamic Self-Consistent Field Theories for Polymer Blends and Block Copolymers	105
	<i>T. Kawakatsu</i>	
1	Introduction . . . . .	105
2	Basic Formalism for Dynamic SCF Theory . . . . .	107
2.1	Diffusion flux . . . . .	108
2.2	Convection flux . . . . .	110
2.3	Flux induced by external fields . . . . .	111
3	Dynamic SCF Theories in Slow Diffusion Regime . . . . .	112
3.1	Formulation . . . . .	112
3.2	Formation process of mesophases of block copolymer melt . . . . .	113
3.3	Dynamics and non-equilibrium domain structures in thin films and near solid surfaces . . . . .	115

3.4	Structural phase transitions induced by external fields . . . . .	117
4	Beyond Diffusion Dynamics — Hydrodynamics, Viscoelasticity and Hybrid Techniques . . . . .	121
4.1	Hydrodynamic effects on domain formation . . . . .	121
4.2	Dynamic SCF with viscoelastic properties . . . . .	124
4.3	Hybrid simulations with particles and fields . . . . .	127
5	Conclusion . . . . .	129
5.	Molecular Dynamics in Crystallization of Helical Polymers: Crystal Ordering and Chirality Selection . . . . .	133
	<i>T. Yamamoto</i>	
1	Introduction . . . . .	134
2	Our Strategies for Simulating Crystallization in Helical Polymers . . . . .	136
3	Molecular Models and Simulation Methods . . . . .	138
3.1	MD simulations . . . . .	138
3.2	MC simulation . . . . .	140
4	Crystallization of the <i>Bare</i> Helix . . . . .	142
4.1	A primary nucleation of a single polymer <i>in vacuo</i> . . . . .	142
4.2	Crystallization of a single polymer on a growth front . . . . .	147
4.3	Order-disorder transition and crystal chirality . . . . .	150
4.4	Development of chiral crystal . . . . .	156
5	Simulations for iPP, a Helical Polymer with Side Groups . . . . .	163
5.1	Collapsing of a single iPP chain <i>in vacuo</i> . . . . .	164
5.2	Crystallization of a single chain with definite chiral recognition . . . . .	166
5.3	Crystallization and polymorph selection . . . . .	170
6	Conclusions . . . . .	175
6.	Interplay of Liquid-Liquid Demixing and Polymer Crystallization . . . . .	179
	<i>W. Hu</i>	
1	Introduction . . . . .	179
2	Theoretical Model . . . . .	182
3	Simulation Techniques . . . . .	184
4	Results and Discussion . . . . .	186
4.1	Liquid-liquid demixing enhanced by crystallizability . . . . .	186
4.2	Crystal nucleation enhanced by prior L-L demixing . . . . .	188

4.3	Crystal nucleation enhanced by prior L-L demixing in the single-chain systems . . . . .	199
5	Perspectives . . . . .	204
7.	Elucidation of Single Molecular Observation of a Giant DNA <i>C.-Y. Shew and K. Yoshikawa</i>	207
1	Polymer Physics Aspects of DNA Conformation . . . . .	208
2	Manipulation and Measurement DNA Conformation In Vitro . . . . .	209
2.1	Condensing agents . . . . .	209
2.2	Single molecular images . . . . .	210
2.3	Limitation of traditional light scattering . . . . .	212
3	All-or-none Conformation Transition of DNA . . . . .	212
3.1	Discrete conformational transition of DNA . . . . .	212
3.2	Chain stiffness and discrete conformational transition . . . . .	213
4	Dynamics of Conformational Relaxation . . . . .	214
4.1	Time dependent conformational behavior . . . . .	215
4.2	Folding and unfolding kinetics . . . . .	216
5	Conformational Hysteresis . . . . .	218
5.1	Characterization of hysteresis . . . . .	218
5.2	Thermodynamics in conformational hysteresis . . . . .	219
5.3	Hysteresis under mechanical forces . . . . .	221
6	Effect of Charge on DNA Conformation . . . . .	224
6.1	Conditions to induce intramolecular segregation . . . . .	224
6.2	Polyelectrolyte analogy . . . . .	224
6.3	Phase diagram of intermolecular and intramolecular segregation . . . . .	225
7	Temperature Effect of DNA Conformation . . . . .	228
7.1	Temperature induced conformational change . . . . .	228
7.2	Competition of smaller ions on compaction . . . . .	230
8	Applications . . . . .	230
	Concluding Remarks . . . . .	233
8.	Theoretical Modeling of Hydrogen Bonding in Macro- molecular Solutions: The Combination of Quantum Mechanics and Molecular Mechanics	237
	<i>J. Ma, N. Jiang and H. Li</i>	
1	Introduction . . . . .	238

2	Fragmentation-Based QM/MM Simulations . . . . .	239
2.1	Solvent models . . . . .	239
2.2	Energy-based fragmentation QM . . . . .	240
2.3	Fragmentation QM/MM: Basic idea and formalisms . . . . .	241
2.4	Fragmentation QM/MM simulations on poly(ethylene oxide) polyethylene . . . . .	245
3	Simulations of Solvated Peptides Using Polarizable Force Field Model . . . . .	248
3.1	Fragmentation-based polarization model . . . . .	249
3.2	Configurations of solvated $\alpha$ -conotoxin GI and its analogues . . . . .	251
4	Concluding Remarks . . . . .	255
9.	Exotic Electrostatics: Unusual Features of Electrostatic Interactions between Macroions . . . . .	265
	<i>A. Naji, M. Kanduč, R. R. Netz and R. Podgornik</i>	
1	Introduction . . . . .	266
2	Scenery . . . . .	268
2.1	Colloids, polymers and membranes: The mesoscopic scale . . . . .	268
2.2	Charges: From industry to biology . . . . .	269
2.3	Theoretical challenge and coarse-grained models . . . . .	271
3	Length Scales in a Classical Charged System . . . . .	272
4	From Mean-Field to Strong Coupling Regime . . . . .	273
4.1	Weak coupling or mean-field regime . . . . .	273
4.2	Strong coupling regime . . . . .	274
5	Interactions between Like-Charged Surfaces . . . . .	276
5.1	WC regime: Repulsion . . . . .	277
5.2	SC regime: Attraction . . . . .	278
6	Counterions with Salt . . . . .	279
6.1	Functional integral formalism . . . . .	279
6.2	Dressed counterions . . . . .	281
6.3	WC dressed counterion theory . . . . .	282
6.4	SC dressed counterion theory . . . . .	282
7	Counterions between Randomly Charged Surfaces . . . . .	286
7.1	General formalism: The replica method . . . . .	287
7.2	Disorder effects in the WC regime . . . . .	288
7.3	Disorder effects in the SC regime . . . . .	288
8	Lessons . . . . .	291

10. Computer Modeling of Liquid Crystals	297
<i>R. Hashim</i>	
1 Introduction . . . . .	297
1.1 What is a liquid crystal? . . . . .	298
1.2 Theoretical approach to understanding liquid crystals . . . . .	301
2 Introduction to the Computer Simulation . . . . .	304
2.1 Computer simulation techniques . . . . .	305
2.2 Simulation limitations . . . . .	306
3 Liquid Crystal Models . . . . .	307
3.1 The lattice class . . . . .	308
3.2 The Gay-Berne class . . . . .	317
3.3 Full atomistic class . . . . .	325
3.4 Conclusion . . . . .	331
11. Drop Dynamics in Complex Fluids	339
<i>J. J. Feng, X. Chen, P. Yue and C. Zhou</i>	
1 Introduction . . . . .	340
2 Partial Coalescence in Polymer Solutions . . . . .	343
2.1 Experimental observations . . . . .	343
2.2 Numerical simulations . . . . .	346
3 Droplet Self-Assembly in Nematic Liquid Crystals . . . . .	352
3.1 Experimental observations . . . . .	352
3.2 Numerical simulations . . . . .	355
4 Summary . . . . .	360
Index	365