CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-86487-9 — Physics of Charged Macromolecules
Murugappan Muthukumar
Table of Contents
More Information

Contents

Preface *page* xiii
Acknowledgments xv

1 Introduction to Charged Macromolecules 1
1.1 General Premise 1
1.2 Chain Connectivity and Long-Ranged Topological Correlation 5
1.3 Scales of Energy, Length, and Time in Charged Systems 6
1.4 Confluence of Electrostatic and Topological Correlations 9
1.4.1 Similarly Charged Macromolecules Can Attract Each Other 9
1.4.2 Ordinary–Extraordinary Transition 10
1.4.3 Reentrant Precipitation 11
1.4.4 Encapsulation of DNA via Complexation 12
1.4.5 Gel Swelling 12
1.4.6 Outlook 14

2 Models of Uncharged Macromolecules 15
2.1 Flexible Chains 15
2.1.1 Mean Square End-to-End Distance 17
2.1.2 Radius of Gyration 17
2.1.3 Segment Density Profile 17
2.1.4 Probability of End-to-End Distance 18
2.1.5 Form Factor 18
2.1.6 Free Energy 19
2.1.7 Tensile Force 20
2.2 Semiflexible Chains 21
2.3 Other Architectures 22
2.3.1 Branched Macromolecules 22
2.3.2 Circular Macromolecules 23
2.4 Excluded Volume Interactions 23
2.5 Chain Swelling 27
2.6 Coil–Globule Transition 30
2.7 Swelling of Randomly Branched Macromolecules 31
2.8 Summary of Size Exponents 32
2.9 Experimental Determination of Size Exponent 33

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-86487-9 — Physics of Charged Macromolecules
Murugappan Muthukumar
Table of Contents
More Information

3 Water, Oil, and Salt 35
3.1 Basics of Electrostatics in Vacuum 35
3.1.1 Force and Electric Field 36
3.1.2 Electric Potential 37
3.1.3 Electrostatic Potential Energy 37
3.2 Dielectric Media 38
3.2.1 Homogeneous Isotropic Linear Dielectrics 39
3.2.2 Entropy of Dielectrics 40
3.3 Water 41
3.4 Dissolution of Salt and Oil in Water 44
3.4.1 Salt 44
3.4.2 Oil and Hydrophobic Effect 45
3.5 Ion Solvation and Born Free Energy 46
3.6 Ion-Pair Formation and Bjerrum Length 49
3.6.1 Release of Bound Water Drives Attraction 49
3.6.2 Bjerrum Length 51
3.6.3 Effect of Ion Size 52
3.7 Dipoles 53
3.7.1 Properties of Simple Dipoles 54
3.8 Dilute Solutions of Strong Electrolytes 58
3.8.1 Poisson–Boltzmann Formalism 59
3.8.2 Debye–Hückel Theory 61
3.8.3 Electrostatic Screening Length (Debye Length) 62
3.8.4 Ion Size and Extended Debye–Hückel Theory 64
3.8.5 Size and Shape of Ion Cloud 66
3.8.6 Free Energy 67
3.8.7 Osmotic Pressure 68

4 Charged Interfaces and Geometrical Objects 70
4.1 Planar Interfaces 71
4.1.1 Salt-Free Solutions 72
4.1.2 Solutions with Salt 74
4.2 Charged Spherical Particles 79
4.3 Charged Cylindrical Assemblies 81
4.3.1 Counterion Distribution in Salt-Free Solutions 81
4.3.2 Counterion Distribution in Solutions with Salt 84
4.4 Line Charge and Manning Condensation 87
4.5 Dielectric Mismatch 89

5 Dilute Solutions of Charged Macromolecules 92
5.1 Introduction 92
5.2 Titration Curves and Charge Regularization 95
5.3 Polyelectrolyte Model Chain and Basic Concepts 100

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-86487-9 — Physics of Charged Macromolecules
Murugappan Muthukumar
Table of Contents
More Information

5.3.1 Excluded Volume Interaction (Hydrophobic Interaction) 102
5.3.2 Electrostatic Interaction 102
5.3.3 Electrostatic Persistence Length 109
5.4 Experimental Results 111
5.5 Simulation Results 113
5.5.1 Radius of Gyration 114
5.5.2 Counterion Adsorption and Effective Charge 116
5.6 Electrostatic Swelling with Fixed Polymer Charge 119
5.6.1 High Salt Limit 119
5.6.2 Low Salt Limit 121
5.6.3 Electrostatic Blob 123
5.6.4 Crossover Formula 124
5.6.5 Electrostatic Stretching of Semiflexible Chains 125
5.7 Self-regularization of Polymer Charge 126
5.8 Coil–Globule Transition in Polyelectrolytes 130
5.9 Apparent Molar Mass, Apparent Radius of Gyration, and Structure Factor 134
5.9.1 Apparent Molar Mass 136
5.9.2 Correlation Hole and Apparent Radius of Gyration 138
5.9.3 Internal Structure 139
5.10 Osmotic Pressure and Donnan Equilibrium 140
5.10.1 Osmotic Pressure of a Dilute Polyelectrolyte Solution 142
5.10.2 Donnan Equilibrium 144
5.10.3 Donnan Membrane Potential 145
5.11 Polyampholytes, Polyzwitterions, and Proteins 146
5.11.1 Polyampholytes 147
5.11.2 Polyzwitterions 149
5.11.3 Intrinsically Disordered Proteins 153

6 Structure and Thermodynamics in Homogeneous Polyelectrolyte Solutions 159
6.1 Introduction 159
6.2 Solutions of Uncharged Macromolecules 162
6.2.1 Flory–Huggins Theory 162
6.2.2 Concentration Fluctuations 166
6.2.3 Scaling Laws 174
6.3 Semidilute and Concentrated Polyelectrolyte Solutions 177
6.3.1 Essentials of Double Screening Theory 177
6.3.2 Effective Interaction and Attraction at Intermediate Distances 180
6.3.3 Correlation Length in Polyelectrolyte Solutions 182
6.3.4 Scattering Function 182
6.3.5 Size of a Labeled Polyelectrolyte Chain 183
6.3.6 Free Energy and Osmotic Pressure 183
6.4 Electrostatically Driven Structure in Salt-Free Polyelectrolyte Solutions 185
6.5 Aggregation of Similarly Charged Polymers 192

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-86487-9 — Physics of Charged Macromolecules
Murugappan Muthukumar
Table of Contents
More Information

7 Dynamics 196
7.1 Introduction 196
7.2 Hydrodynamic Interaction 200
7.3 Dilute Solutions of Colloidal Particles, Macroions, and Folded Proteins 202
7.3.1 Einstein's Electrophoretic Mobility 202
7.3.2 Hückel Theory 204
7.3.3 Henry Theory 206
7.3.4 Helmholtz–Smoluchowski Theory 207
7.3.5 Electroosmotic Flow 208
7.3.6 Zeta Potential 210
7.3.7 Mobility through a Nanopore 211
7.4 Phenomenology of Dynamics of Polyelectrolyte Solutions 213
7.4.1 Diffusion and Relaxation Time 214
7.4.2 Ordinary–Extraordinary Transition 216
7.4.3 Electrophoretic Mobility 219
7.4.4 Viscosity 219
7.5 Models of Dynamics of Uncharged Polymers 222
7.5.1 Rouse Dynamics 225
7.5.2 Zimm Dynamics 230
7.5.3 Reptation Model 233
7.5.4 Entropic Barrier Model 238
7.6 Dilute Polyelectrolyte Solutions 242
7.6.1 Translational Friction Coefficient 242
7.6.2 Electrophoretic Mobility 243
7.6.3 Coupled Diffusion Coefficient 245
7.6.4 Intrinsic Viscosity and Modulus 249
7.7 Semidilute Polyelectrolyte Solutions 250
7.7.1 Tracer Diffusion Coefficient 254
7.7.2 Electrophoretic Mobility 254
7.7.3 Cooperative Diffusion Coefficient 255
7.7.4 Coupled Diffusion and Ordinary–Extraordinary Transition 256
7.7.5 Viscosity 261
7.8 Entangled Solutions 264
7.9 Conductivity of Polyelectrolyte Solutions 265
7.10 Dielectric Relaxation 267
7.11 Polymer Translocation 269
7.11.1 Polymer Capture through a Barrier 273
7.11.2 Kinetics of Translocation 275
7.12 Topologically Frustrated Non-diffusive Dynamics 277

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-86487-9 — Physics of Charged Macromolecules
Murugappan Muthukumar
Table of Contents
More Information

8 Self-Assembly and Phase Behaviors 279
8.1 General Premise 279
8.2 Liquid–Liquid Phase Separation in Solutions of Uncharged Polymers 282
8.2.1 Concentration Fluctuations and Landau–Ginzburg Theory 287
8.3 Coulomb Criticality in Electrolyte Solutions 291
8.3.1 Free Energy 292
8.3.2 Instability and Criticality 292
8.4 Phase Behavior of Polyelectrolyte Solutions 294
8.4.1 Salt-Free Polyelectrolyte Solutions 295
8.4.2 Polyelectrolyte Solutions with Salt 298
8.4.3 Charge Regularization: Daughter Phases Have Different Charge Densities 300
8.4.4 Concentration Fluctuations and Ginzburg Criterion 302
8.5 Kinetics of Phase Separation 303
8.5.1 Spinodal Decomposition 304
8.5.2 Nucleation and Growth 307
8.5.3 Interlude of Aggregation in Phase Separation 308
8.6 Micellization and Microphase Separation 310
8.6.1 Self-Assembly of Charged Diblock Copolymes in Solutions 311
8.6.2 Microphase Separation 316
8.7 Isotropic–Nematic Transition in Solutions of Charged Rods 322
8.8 Proteins, Fibrillization, and Membraneless Organelles 326
8.8.1 Fibrillization 327
8.8.2 Membraneless Organelles 336

9 Adsorption, Complexation, and Coacervation 339
9.1 Introduction 339
9.2 Adsorption 340
9.2.1 Adsorption at a Planar Surface 343
9.2.2 Adsorption at Spherical Surfaces 347
9.3 Charged Brushes 349
9.3.1 No-Salt Limit 350
9.3.2 High-Salt Limit 352
9.3.3 Disjoining Pressure 353
9.3.4 Density Profile 353
9.4 Genome Packaging in Viruses 354
9.5 Intermolecular Complexation 359
9.5.1 Counterion Release Drives Complex Coacervation 362
9.5.2 Competitive Substitution in Intermolecular Complexes 363
9.6 Coacervation 366
9.6.1 Voorn–Overbeek Theory 368
9.6.2 Dipolar Theory of Coacervation 370
9.7 Membraneless Organelles 373

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-86487-9 — Physics of Charged Macromolecules
Murugappan Muthukumar
Table of Contents
More Information

10 Gels 376
10.1 Model Gel and Definitions 378
10.2 Free Energy and Osmotic Pressure of Gels 380
10.2.1 Free Energy of Mixing 381
10.2.2 Electrostatic Interaction Energy 381
10.2.3 Free Energy of Deformation 382
10.2.4 Osmotic Pressure from Mobile Ions and Donnan Equilibrium 385
10.2.5 Fluctuations 387
10.3 Equilibrium of Isotropically Swollen Gels 387
10.3.1 Salt-Free Gels 388
10.3.2 Gels with High Salt 388
10.3.3 Crossover Behavior with Salt 390
10.4 Gel Swelling under Confinement 391
10.4.1 One-Dimensional Swelling 392
10.4.2 Two-Dimensional Swelling 393
10.5 Gel Swelling under Tension 394
10.5.1 Solvent Uptake with Gel Stretching 394
10.5.2 Length–Force Relation 395
10.6 Elasticity of Swollen Gels 397
10.6.1 Simple Elongation 397
10.6.2 Simple Shear 398
10.6.3 Osmotic Bulk Modulus 401
10.6.4 Poisson Ratio 402
10.7 Dynamics of Charged Gels 403
10.7.1 Elasticity Equations 403
10.7.2 Determination of Gel Moduli Using Scattering Experiments 406
10.7.3 Coupling between Gel Dynamics and Counterion Dynamics 412
10.7.4 Scaling Laws 413
10.8 Kinetics of Gel Swelling 415
10.9 Phase Transitions in Gels 416
10.9.1 Critical Point at High Salt Concentrations 420
10.9.2 Critical Point for Salt-Free Gels 421
10.10 Charge Regularization 425
10.10.1 Overcharging and Reentrant Volume Transition 431
10.11 Summary 432

11 Epilogue 434
Appendix 1 436
Appendix 2 437
Appendix 3 442
Appendix 4 445
Appendix 5 447
Appendix 6 451

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-86487-9 — Physics of Charged Macromolecules
Murugappan Muthukumar
Table of Contents
More Information

Appendix 7 471
Appendix 8 473
Appendix 9 476
Appendix 10 478
References 483
Index 502

© in this web service Cambridge University Press & Assessment www.cambridge.org