

## Physics of Charged Macromolecules

Charged molecules permeate all aspects of our modern lives including food, health care, and water-based technologies. As a concise introduction to the physics of charged macromolecules, this book covers the basics of electrostatics as well as cutting-edge modern research developments. This accessible book provides a clear and intuitive view of concepts and theory, and features appendices detailing mathematical methodology. Supported by results from real-world experiments and simulations, this book equips the reader with a vital foundation for performing experimental research. Topics include living matter and synthetic materials including polyelectrolytes, polyzwitterions, polyampholytes, proteins, intrinsically disordered proteins, and DNA/RNA. Serving as a gateway to the growing field of charged macromolecules and their applications, this concept-driven book is a perfect guide for students beginning their studies in charged macromolecules, providing new opportunities for research and discovery.

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# Physics of Charged Macromolecules

Synthetic and Biological Systems

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## Preface

Charged macromolecules constitute the vocabulary used by Mother Nature to express life as we know it. These molecules are also abundant in the synthetic world. Yet, understanding the behavior of charged macromolecules is one of the grand challenges of the biological and physical sciences. The difficulty of this challenge lies in several long-range forces operating simultaneously that endow assemblies of charged macromolecules with amazing functions. The electrostatic forces, topological correlations emanating from macromolecular connectivity, and hydrodynamics are all long-ranged. These aspects collectively guide the structure, dynamics, and movement of individual macromolecules and their assemblies. In view of the prevalence of charged macromolecules in nature, extensive phenomenology has been cultivated during the past many decades. The rich collective behaviors of charged macromolecules are unique to the presence of charges and deviate significantly from those of uncharged macromolecular systems. In efforts to understand these behaviors, there has been extensive theoretical effort during the past seven decades with variable success. More and more theories are being vigorously pursued, with different levels of assumptions and approximations, in order to obtain a comprehensive description of the behavior of charged macromolecules.

This complicated field of charged macromolecules inevitably demands highly sophisticated mathematical techniques accompanied by clear physical pictures. The goal of this book is to focus on the most important concepts pertinent to electrolyte solutions, charged macromolecules, and their assemblies. Heavy mathematics and fine details of theories are relegated to the original literature. I am painfully aware that I have left out many interesting developments particularly in theoretical aspects. Most of the material in this book deals with fundamentals and general concepts that are yet to enter textbooks.

This book is an introduction to the vast field of charged macromolecules practiced by biologists, physicists, chemists, and chemical engineers. It is written at the level of an entering graduate student who is interested in the burgeoning fields of living matter, soft matter physics, polyelectrolyte physics, and biotechnology. The book is structured in a manner that it provides a gateway to a large number of topics at the center of the physics of charged macromolecules. The goal is to provide a common language of fundamental concepts to a broader audience, independent of the expertise of the reader. Creating a common conceptual framework in such a difficult subject for use by a diverse readership is not an easy task. However, I have attempted to start from the

basics of charged and uncharged polymers, and then I have combined these concepts to describe the collective behavior of charged systems. Effort is made to make the discussion qualitative and concept based. Technical details of a few important concepts are provided in appendices. Highly sophisticated mathematical details are referred to original publications.

The outline is as follows: After an exposure to the scope of the topics in Chapter 1, the second chapter provides a synopsis of models of uncharged polymer chains in isolation and experimental results in dilute solutions. Chapter 2 is a convenient introduction to readers who might be interested solely in basic polymer physics. The next two chapters, Chapters 3 and 4, deal with the basics of electrostatics, dielectric media, interactions among electrolyte ions, and the nature of electrolyte solutions with physical boundaries. Chapter 5 is devoted to a survey of experimental results in dilute solutions of charged macromolecules and various theoretical approaches to comprehend these facts. Chapter 6 describes how the fundamental principles developed in dilute solutions are modified by crowding of charged macromolecules in homogeneous nondilute solutions. This situation has been a long-standing challenge to understand requiring advanced theoretical apparatus. Readers interested in biological systems in dilute conditions can skip this chapter without losing the thread of concepts. The dynamics of solutions of charged macromolecules is dealt with in Chapter 7. This chapter, along with Appendix 6, constitutes a separate mini-book of their own and deals with the dynamics and mobility of charged rigid particles and flexible macromolecules. Chapter 8 deals with the fundamentals of liquid–liquid phase separation in solutions of charged macromolecules after addressing the situation with uncharged macromolecules. Micellization, fibrillization, and microphase separation are also dealt with in Chapter 8. Applications of the various concepts developed in the above chapters to the phenomena of adsorption, virus packing, and coacervation are presented in Chapter 9. The final chapter is on charged gels, which are ubiquitous in health care and other industries. The gap between what we understand today and what needs to be accomplished in the future is briefly mentioned in the Epilogue.

I hope the readers will benefit from this introduction to the field and implement the main concepts given here in their own journeys with charged macromolecules.

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I also gratefully acknowledge support from the National Science Foundation for my research on charged macromolecules. Without such support, this book would not have been a possibility. I am also indebted to many collaborators outside my laboratory. In particular, it is a pleasure to thank Professor Manfred Schmidt for his friendship and numerous stimulating discussions on the intricacies of polyelectrolyte behavior.

Finally, it is my greatest pleasure to thank my wife Lalitha for all support she has provided throughout my career. During the difficult time of writing this book, I was fortunate to spend time with my grandson Kanna who inspired boundless energy, imagination, and purity of thought. I am immensely grateful to him for support and play.

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