Electrostatics of Soft and Disordered Matter

“This is a timely and illuminating volume, reviewing the state of the art of Coulombic fluids, and shedding some light on the counter-intuitive phenomena that emerge from Coulombic interactions. The book is in particular interesting because it reviews the fundamental role played by Coulombic interactions when macromolecules are dissolved in an aqueous milieu. An up-to-date introduction of the subject as well as advanced topics that will be welcome by students and researchers alike.”

Prof. David Andelman
Tel-Aviv University, Israel

Recently there has been a surge of activity to elucidate the behavior of highly charged soft matter and Coulomb fluids in general. Such systems are ubiquitous especially in biological matter where the length scale and the strength of the interaction between highly charged biomolecules are governed by strong electrostatic effects. Several interesting limits have been discovered in the parameter space of highly charged many-particle Coulomb matter where analytical progress is possible and completely novel and unexpected results have been obtained.

This book fills the void that exists in the literature, cross-pollinates different theoretical and simulation approaches with new experiments, and develops a unified perspective on the counter-intuitive features of the electrostatic interactions, which to a large extent determine the stability and conformations of most important biological macromolecules. The scope of the book is thus to present current advances in the field of Coulombic (bio)colloidal systems, upgrading the previous literature that summarized the state of the art of the field about 15 years ago.

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Electrostatics of Soft and Disordered Matter
Electrostatics of Soft and Disordered Matter

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Preface

The last relatively complete compendium of the electrostatics of soft matter, edited by C. Holm, P. Kekicheff, and R. Podgornik, saw the light of day in the distant 2001, immediately following the Les Houches École de Physique NATO Advanced Study Institute’s school on “Electrostatic effects in soft matter and biophysics,” which itself grew out of a workshop organized by W. Gelbart, V. A. Parsegian, and P. Pincus at the Kavli Institute for Theoretical Physics (KITP) in Santa Barbara, USA, in 1998 with a similar theme. The destiny of the present volume had a similar time course: from an idea at the 2008 KITP workshop “Theory and Practice of Fluctuation-Induced Interactions,” organized by T. Emig, M. Kardar, V. A. Parsegian and R. Zandi, to the CECAM workshop “New Challenges in Electrostatics of Soft and Disordered Matter,” organized by the editors of this volume, at the University of Toulouse III, France, in 2012. Since we were able to gather in Toulouse most of the leading researchers in the field, we decided that the time was appropriate for a new compendium of the state of the art in Coulomb fluids that we can offer to the readers in order to foster the development and promote the education in this exciting and rapidly growing field.

All the 27 chapters of this book contain illuminating and well-written mini-reviews of recent work by some of the foremost scientists working in these fields today. The introductory chapter was written by V. A. Parsegian, who provided some personal reminiscences and historical insights, followed by five distinct blocks of chapters with self-explanatory titles: I. Coulomb Fluids: From Weak to Strong Coupling, II. Ions at Interfaces and in Nanoconfinement, III. Complex Colloids, IV. Biological Systems and Macromolecular Interactions, and V. Disorder Effects in Coulomb Interactions. We assembled contributions that would adequately reflect the various
aspects and colorful variety of different methodologies used today to describe the properties of thermal systems with long-range Coulomb interactions. Because of our insistence that the chapters be written with students in mind, we are convinced that the book will be useful to undergraduate as well as graduate students who wish to learn about the intricacies of these systems with sometimes very counter-intuitive behaviors, while the more seasoned researchers will benefit from an up-to-date account of both the experimental phenomenology and the rich variety of theoretical approaches to Coulomb fluids.

While the preparation of this book at the end of 2013 was in full swing, we learned the sad news that N. G. Van Kampen passed away. We deem that it is appropriate to mention here his seminal contribution to the understanding of (thermal) fluctuation interactions in Coulomb systems, addressed in several chapters of the present book within the context of the so called “weak-coupling theory”. Van Kampen’s “heuristic” mode summation approach to (Casimir) fluctuation interactions, proven to be actually exact by V. L. Ginzburg and Y. S. Barash in the eighties, was later generalized by V. A. Parsegian, B. W. Ninham, and G. H. Weiss to finite temperatures and shown to be equivalent to the Lifshitz theory.

At the end we would like to thank all the contributors of this volume for their fine work and personal involvement that made the publication of this book possible. We would also like to thank the helpful staff at Pan Stanford Publishing, as well as CECAM for funding the workshop “New Challenges in Electrostatics of Soft and Disordered Matter” at University of Toulouse III in 2012. We would like to specifically thank Dr. Valerie Blanchet, who took time off from her research on femtosecond quantum chemistry, to help us in the organization of our largely classical conference.

David S. Dean
Jure Dobnikar
Ali Naji
Rudolf Podgornik
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Introduction

The field of electrostatically mediated interactions in classical systems has a long and illustrious history. At its inception it was a discipline firmly implanted as a part of physical chemistry and many of the early results are today given as examples of the development of the statistical physics of interacting systems. Much theoretical progress has been made since then, but as with all three-dimensional interacting particle systems, the exact solution of the statistical mechanics of a system involving mobile charges (Coulomb fluid) is still absent. Electrostatic interactions have however played a central role in the analysis of interacting particle systems. With respect to other systems, the presence of long-range Coulomb interactions leads to interesting physical and mathematical properties of these systems—they exhibit screening, sum rules, and have elegant field theoretical formulations that enable their analysis in both weakly and strongly charged limits. In particular there has been a recent surge of activity in order to elucidate the details of the behavior of charged soft matter and Coulomb fluids in the limit of strong coupling, which emerged as a new regime, apart and distinct from the well-known Poisson–Boltzmann or weak coupling regime. These two limits and the corresponding regimes in the behavior of highly charged many-particle Coulomb matter are important also because they allow for very illuminating analytical progress to be made. Systems of this type are ubiquitous in soft matter; especially in bio-matter, where they set the length scale and strength of the interaction between highly charged biomolecules. In parallel to theoretical progress in the field, the development of biophysics and the emergence of soft condensed matter has lead to the experimental study of systems where electrostatic effects are dominant and also variations in temperature and salt concentration.
(quantities which are relatively easy to tune experimentally) lead to rich and interesting behavior.

The field of electrostatic effects is therefore particularly important today because electric charges are commonplace in soft and biological systems. Most soft materials such as polymers, colloids, proteins and membranes acquire surface charges when dissolved in water and release small mobile ions into the solution. They are easily deformed by potentials comparable to thermal energy and thus electrostatic forces constitute a prominent factor determining the structure and properties of these materials in various applications. In industry, charged macromolecules are used, due to their high water solubility, in a whole range of applications such as in design and processing of non-toxic environmentally friendly materials. In biology, electrostatic effects come into play in many examples such as in the DNA packaging in the cell nucleus and also in the formation of DNA condensates as observed, for instance, in bacteriophages that can inject their DNA into a target cell forming therein a torus-like DNA condensate with a diameter of up to a few hundred nanometers. Electrostatic forces in this latter example enter in a counterintuitive fashion, leading to strong attraction between like-charged segments of DNA. Recent studies show that such strongly coupled structures are dominated by attractive correlation forces induced by counterions between juxtaposed macromolecular surfaces and they emerge when the surfaces are highly charged and counterions are multivalent.

With all these recent developments in mind, the editors of this book organized a CECAM sponsored workshop held in Toulouse, France, in the Spring of 2012. The idea was to bring together both experimentalists and theorists working on these new challenges in electrostatics of soft and disordered systems to present and discuss their recent results. The interest in the workshop was intense and in addition to the invited speakers, many other scientists also attended it. At the end of the workshop the general mood was that we should try to assure the legacy of this workshop by preparing a volume of proceedings that would serve to give a snapshot of the state of the art at that precise moment and point out the open questions and challenges in the field.
The contributions to this book naturally fell into five distinct areas that make up the five parts of this book. One is the low-temperature Wigner crystal Ansatz, which starts with the zero-temperature ground state corresponding to crystallization of counterions in the 2D Wigner lattice close to the surfaces. Another is a limiting strong-coupling approach based on the functional-integral representation of the partition function. Both approaches yield an effective interaction between two apposed equally charged surfaces that can be counter-intuitively attractive. Furthermore, fluctuations about the mean-field (Poisson–Boltzmann) limit have also been studied and have been shown to generalize the concept of the temperature-dependent Casimir interactions. Certain aspects of realistic Coulomb systems are shared by exactly soluble one-dimensional and two-dimensional Coulomb systems and help our understanding of various approximation in order to assess their applicability in well-controlled situations. In most realistic systems, however, there are multiple-length scales precluding their analysis within a single regime. It is for this reason that this book in which experts have presented their various and different approaches is timely in order to realize how these theories can be linked with each other to describe complex systems containing a number of regimes. Dielectric properties of the surfaces and interfaces have been treated at the continuum level as well as various levels of other more microscopic approaches. In particular, the granularity of the solvent introduces phenomena which, while known experimentally for many years, are only now becoming the focus of sophisticated simulation approaches as well as coarse-grained semi-analytical approaches that take various aspects of the non-homogeneous nature of interfaces into account. In this context, one should particularly mention the hydration interactions and the ion-specific effects where we seem to be on a good track to finally give a theoretical perspective to various experimentally well-studied phenomena. Many-body aspects of electrostatic interactions with mobile charges in complicated mixed solvents as well as dielectric response of polyelectrolyte solutions introduce novel features in the theories of electrostatic interactions. These aspects are furthermore developed in the context of biological systems. Solvation interactions and specific features of electrostatic interactions in
systems containing biological macromolecules introduce additional refinements of the charge distribution models, pertaining either to the fixed charges of the macromolecular surfaces or indeed to the counterions themselves. These generalizations introduce very specific features to interactions between such quintessential biological macromolecules as DNA. While charge distributions of various fixed magnitudes and geometries certainly cover many of the real-world charged interfaces, one nevertheless has to deal also with structural charge disorder, which will almost invariably be present. Relaxing the Ansatz of a uniform surface charge density and allowing for a disordered component characterizing the charge distribution has led to emergence of new phenomena leading to extremely long-range interaction potentials between disordered charge distributions that can be compared with intriguing features of recent careful experiments.

All the chapters of this book contain illuminating and well written mini-reviews of recent work by some of the foremost scientists working in these fields today. The contributors have paid particular attention to the pedagogy of their chapters so that the book can provide a very up-to-date introduction of the subject to young scientists as well as more established scientists who wish to learn about new developments in the field.