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José Antonio Fornés

Electrical Fluctuations in Polyelectrolytes

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ISSN 2191-5407 ISSN 2191-5415 (electronic)
SpringerBriefs in Molecular Science
ISBN 978-3-319-33839-2 ISBN 978-3-319-33840-8 (eBook)
DOI 10.1007/978-3-319-33840-8

Library of Congress Control Number: 2016940063

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Preface

*To my wife, Nélide, who was always a source of love and inspiration. In memory
“Science is an evolution of ideas and approximations,” José A. Fornés, 1998.*

The importance of estimating fluctuations in physics is because they contain a lot of information: Electromagnetic fluctuations are the origin of London (van der Waals) forces (1937) between molecules and Lifchitz forces (1956) between macro-objects. Protonic fluctuations are the origin of Kirkwood and Schumaker forces (1952) between molecules and pH fluctuations (Fornés et al. 1999). Also protonic fluctuations could be the cause of the dielectric increment of proteins in solution. Local electrical fluctuations can influence chemical reactions. Polyelectrolytes are present in almost all the biological systems. In order to understand how these systems work, it is important to know the size of their electrical fluctuations. The present book represents the work the author has performed on this subject while he was professor at the Institute of Physics of Goiás University. I am grateful to my many friends and colleagues. I would like especially to acknowledge the help I received from Amando S. Ito, Joaquim Procopio, and José Nicodemos T. Rabelo, who influenced very much my scientific career, and also the help I received from Salviano de Araújo Leão, who was always ready to help me with computational softwares. Also I want to acknowledge the help I received from Daniel Leite in the design of the figures. Also, I would like to thank to Luis Furtado, Springer’s editor in Brazil, whose perfect orientation and cordial treatment made this book reality. It has been a considerable pleasure to work with him. Finally, I want to express my gratitude to Susan Westendorf, my book project coordinator, Springer Nature, in New York, who always was ready to give a hearty assistance, related to the book production. *March 2016, José Antonio Fornés Instituto de Física UFG, Brazil.* I want to express my recognition to Sarumathi Hemachandirane, Project Manager Publishing SPi Global in India and her Team, for such a careful and perfect job in the production of the book.

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Chapter 1

The Electrical Capacitance, the Link to the Electrical Fluctuations

Abstract In this chapter, we develop a method in order to estimate the electrical fluctuations in small systems. The method consists in knowing the electrical capacitance that emerges as a consequence of the processes or the system's interfaces. We use results given by the fluctuation-dissipation theorem in the classical limit. Estimating the electrical capacitance is important because it is the link to the knowledge of the fluctuation of several physical quantities, voltage and field fluctuations, dipole moment, pH, and charge, and also to knowledge of the polarizability and the dielectric dispersion of colloidal and polyelectrolytes systems.

Keywords Charge fluctuation capacitance • Small systems • Electrical fluctuations

1.1 Electrical Fluctuations

The importance of local field fluctuations in biological systems was raised by several authors: Weaver and Astumian [21] have presented a calculation of the effects of weak fields upon cells. Procopio and Fornés [16], using the fluctuation-dissipation theorem (FDT), have presented a calculation of the voltage fluctuations across cell membranes. Protonic fluctuations could be the cause of the dielectric increment of proteins in solution [11, 20]. For fluctuations of ion distribution in colloid and polyelectrolyte solutions, see, for instance, [4, 13, 14], see also the next chapters. Also local fluctuations can influence chemical reactions, see [1]. Oosawa [15] has also calculated the magnitude of fluctuating voltage and field across different points of an electrolyte solution constituted of point ions using the method of the mode expansion [1, 3–6, 13–15, 18, 19]. Also Brownian motors are small physical micro- or even nano-machines that operate far from thermal equilibrium by extracting the energy from both thermal and non-equilibrium fluctuations in order to generate work

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