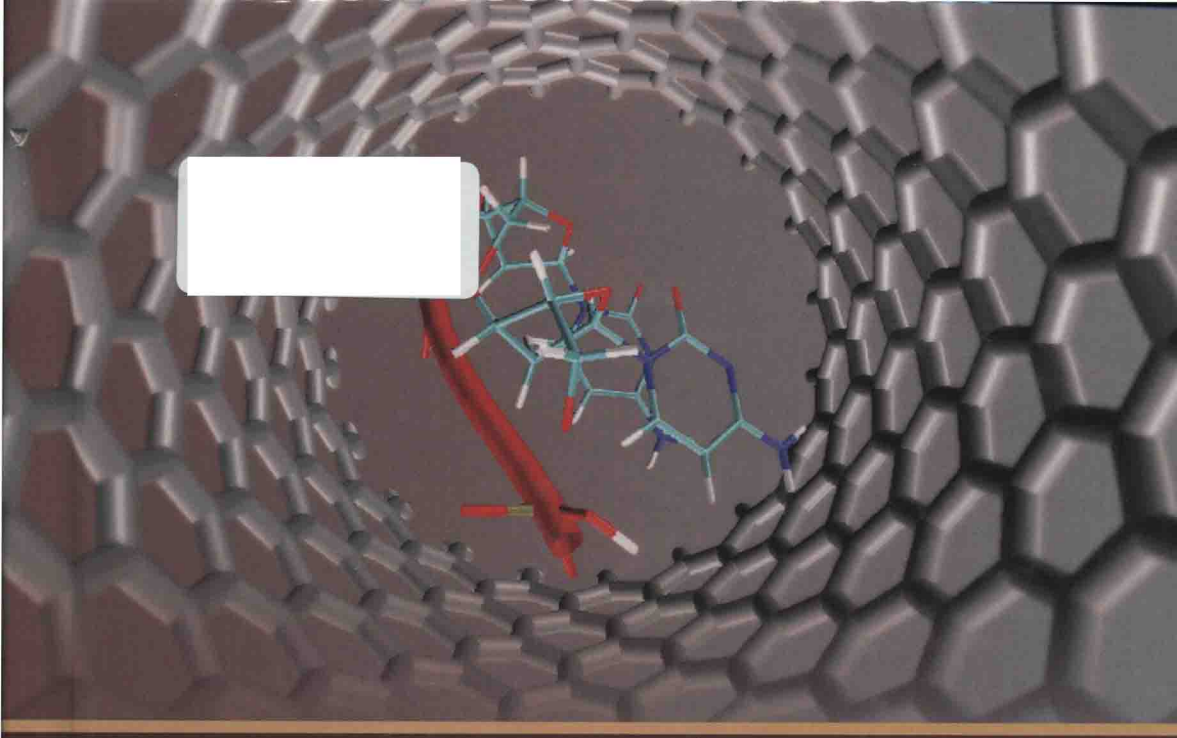


# Nanobiophysics

## Fundamentals and Applications

edited by Victor A. Karachevtsev

# Nanobiophysics

## Fundamentals and Applications

edited by

Victor A. Karachevtsev



Pan Stanford Publishing

*Published by*

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com
Web: www.panstanford.com

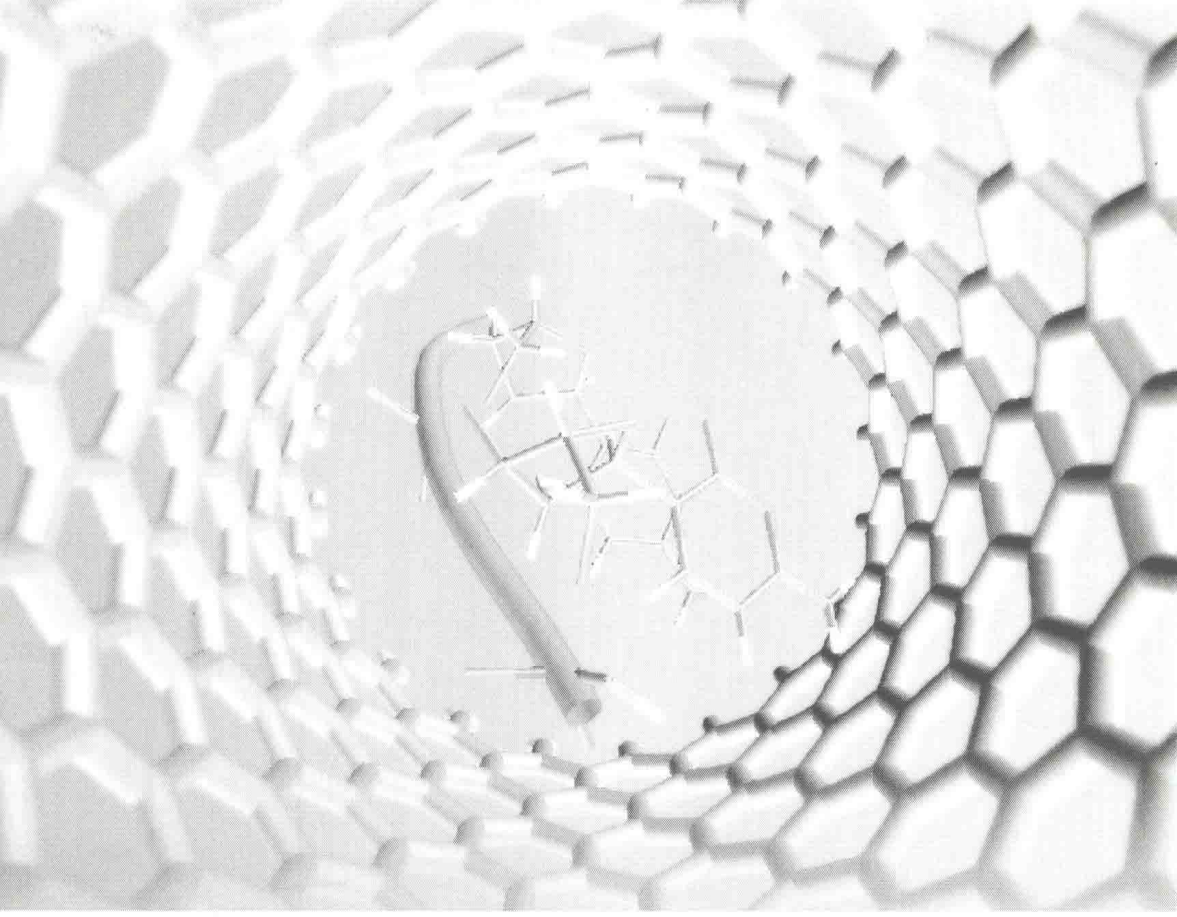
**British Library Cataloguing-in-Publication Data**
A catalogue record for this book is available from the British Library.

**Nanobiophysics: Fundamentals and Applications**



ISBN 978-981-4613-96-5 (Hardcover)
ISBN 978-981-4613-97-2 (eBook)

Printed in the USA



# Nanobiophysics

# Preface

The recent rapid development of nanoscience and nanotechnology has promoted new types of multidisciplinary efforts and has initiated new branches of science. Nanobiophysics is one of them. Nanobiophysics operates at the interface of physics, biology, chemistry, nanotechnology, and medicine. Nanobiophysics research focuses on the manipulation of single biomolecules, development of interfaces between single biomolecules and single nanoparticles, creation of new nanobiostructures and study of their properties, bio-diagnostics and the development of biological sensing devices, and application of nanobiophysics in medicine. Nanophysics researchers often combine basic research and fundamental studies with practical applications. The basic motivation of these investigations includes elucidation of the fundamental mechanisms of biological processes at the molecular level and interfacing this knowledge with various medical and nanobiotechnology applications.

This book, titled *Nanobiophysics: Fundamentals and Applications*, introduces the field of nanobiophysics through 12 reviews written by 35 experts in the field. The aim of the reviews is not to provide a comprehensive description of all scientific directions in the field of nanobiophysics but rather to concentrate on some selected topics related to the physics of biomolecular nanosystems, nanobiohybrids involving nanocarbons, biomolecules deposited on nanoparticles, and nanostructured surfaces. The reviews also cover some topics concerning the development of sensors and of nanoscale scaffolds for the delivery of therapeutic nucleic acids to cells. Many biological systems have unique and unusual properties (e.g., proteins, enzymes, biopolymers) and their molecular sizes place them within the category of nanosystems. The development of nanoscience gives new impulse to investigate these systems with the methods provided by nanobiophysics. This opens new perspective for nanoarchitecture design, which exploits the unique properties of bionanosystems.

Among the various biological nanostructures, DNA/RNA systems attract special attention due to their fundamental role in living matter. In this book, three of the reviews describe the recently acquired insight into the structural dynamics of nucleosomal DNA and the structures and the interactions between components of nanobiohybrids formed by DNA/RNA and single-walled carbon nanotubes. These nanotube-based systems are considered as possible siRNA delivery systems. Their rather weak interaction with RNAs makes them promising tools for applications in gene silencing for gene therapy and in gene functional analysis.

Some reviews in the book describe unique experimental physical methods that are used to study nano-size biostructures. The methods include structure diagnostics of liquid nanosystems by small-angle scattering, a liquid-crystal ordering approach to model lipid membranes, analysis of nano-sized complexes of bioorganic molecules in low-temperature matrixes by means of vibration spectroscopy, and mass spectrometric diagnostics of interactions between biologically active redox-sensitive dyes and nanomaterials. Applied aspects of nanobiophysics are presented in two chapters of the book, in which the state of the art in the fabrication of gas sensors focusing on breath gas detection and of the polycyclic aromatic hydrocarbon sensor.

There are reviews in the book that present results of theoretical investigation of nanobiosystems performed with quantum-mechanical and molecular modeling methods (such as the molecular dynamics method). The use of these two methods allows the elucidation of the very complex functioning of such biosystems as protein, enzymes, and DNA. This in turn helps in fabricating nanohybrids of these systems with inorganic nanostructures. These hybrids can be used in the development of new biosensors and of new molecular nanoarchitectures, for cell delivery of drugs. The theoretical calculations also reveal the molecular nature of the bonding and non-bonding interactions in nanobiosystems. They also provide information on the bonding energies and on the structures of the bonding sites.

Another fundamental research described in the book is devoted to the theoretical consideration of the kinetic treatment of relaxation and fluctuation processes accompanying the environment-induced transitions in biomolecules on the micro- to nanoscales. In this review, two unusual nanoscale effects are presented, namely, the

temperature "independent" decay for transitions between the quasi-isoenergetic levels by virtue of their fluctuations and the "negative" cooperativity for sigmoid distribution of meta-stable state population because of the system irreversibility. Recent efforts in the creation of the theoretical model to describe the polymer-mediated interactions among nanoparticles, which play a key role in many biological and technological processes, are also reviewed.

This book is written by experts in different fields of biophysics, material science, biochemistry, and bioengineering. Each chapter can be read as a separate mini-book on a particular subject. I encourage the reader to use this book as an introduction to nanobiophysics and its different subfields. The book can benefit both students, by introducing them to this new fundamental and modern branch of science, and researchers from other disciplines by describing to them the ways in which their research can be interfaced with studies of nanobiosystems.

I would like to thank all the authors accepting the invitation to contribute to this book for their diligence in the review preparation. My thanks to the editorial staff at Pan Stanford Publishing for their assistance in the publication of this book.

**Victor A. Karachevtsev**
B. Verkin Institute for Low Temperature Physics and Engineering
The National Academy of Sciences of Ukraine, Kharkov, Ukraine

# Contents

*Preface* xiii

**1. Quantum-Mechanical Investigations of Noncovalent Interactions of Carbon Materials** **1**

*Stepan G. Stepanian, Maksym V. Karachevtsev, and Ludwik Adamowicz*

1.1 Introduction 2
1.2 Methods 4
1.2.1 The Hartree–Fock Method 4
1.2.2 The MP2 and Post-MP2 Methods 5
1.2.3 Density Functional Theory 6
1.2.4 Basis Sets 8
1.2.5 Surface Models 8
1.3 Physisorption of Nucleic Acid Bases on Carbon Nanotubes and Graphene 10
1.3.1 Structure and Interaction Energies 11
1.3.2 Stability Order 14
1.3.3 Base Pairs 14
1.4 Aromatic Amino Acids 17
1.5 $\pi$-Conjugated Hydrocarbons 20
1.6 Binding of Charged Species 25
1.7 Conclusions 26

**2. Hybrids of siRNA with Carbon Nanotubes as RNA Interference Instruments** **33**

*Evgeny K. Apartsin, Marina Yu. Buyanova, Darya S. Novopashina, and Alya G. Venyaminova*

2.1 Introduction 34
2.2 Hybrids of siRNA with Carbon Nanotubes: Formation and Properties 35

2.3 Cellular Uptake of CNTs and Their Hybrids with Nucleic Acids 38
2.4 siRNA Delivery *in vitro* 40
2.5 siRNA Delivery *in vivo* 44
2.6 Conclusions and Perspectives 48

**3. Single-Walled Carbon Nanotubes Interfaced with DNA/RNA 59**

*Maksym V. Karachevtsev and Victor A. Karachevtsev*

3.1 Introduction 60
3.2 SWNT:DNA Hybrids: Structures and Energy Interaction 61
3.3 Encapsulation of DNA inside Nanotube 68
3.4 DNA Sequencing by Translocation through SWNT Nanopores 73
3.5 Recognition Ability of DNA for Carbon Nanotubes 74
3.6 Carbon Nanotube: DNA Nanoarchitectures 76
3.7 Summary and Future Prospects 83

**4. Nucleosome as an Example of a Nanosystem Formation: Structural Dynamics of Nucleosomal DNA 95**

*Mariya Yu. Zhitnikova, Olena P. Boryskina, and Anna V. Shestopalova*

4.1 Introduction 96
4.2 Nucleosome as the First Level of DNA Compactization 97
4.2.1 Structural Levels of DNA Compaction in Eukaryotic Cells 98
4.2.2 Nucleosome Structure: Histone Core 100
4.2.3 Interaction of Nucleosomal DNA with Histone Core 102
4.3 Nucleosome Formation 104
4.3.1 Nucleosome Stability 104
4.3.2 Nucleosome Self-Assembly 106
4.4 The Structural Features of Nucleosomal DNA 109
4.4.1 Deformation of Nucleosomal DNA 109
4.4.2 Conformational Dynamics of DNA Sugar-Phosphate Backbone 112

4.5 Structural Dynamics of Nucleosomal DNA Sugar-Phosphate Backbone 114
4.5.1 Data Set of Nucleosome Crystallographic Structures 114
4.5.2 Frequency and Sequence-Specificity of Transitions of the $\alpha/\gamma$ Angles to Alternative States 115
4.5.3 Distribution of Nucleotides with Alternative Conformations of $\gamma$ Angle on Nucleosomal DNA 117
4.6 Concluding Remarks 120

**5. Structure Diagnostics of Biorelevant Associates and Complexes in Liquid Nanosystems by Small-Angle Scattering 129**

*Viktor Ivanovich Petrenko, Leonid Anatolievich Bulavin, Mikhail Vasilievich Avdeev, and Peter Kopcansky*

5.1 Introduction 130
5.2 Small-Angle Scattering as a Powerful Method for Structure Diagnostic of Liquid Nanosystems 135
5.3 Structure and Interaction in Magnetic Fluids 137
5.3.1 Structure of Aqueous Ferrofluids 137
5.3.2 Stabilization Features of Magnetic Fluids 141
5.4 Internal Structure of Protein Amyloid Solutions 143
5.4.1 SANS on Amyloids Protofilaments 143
5.4.2 Complementary AFM Studies of Amyloids Protofilaments 145
5.5 Structure Characterization of Magnetoferritin Aqueous Systems 148
5.6 Conclusions 153

**6. Liquid Crystal Ordering and Nanostructuring in Model Lipid Membranes 163**

*Longin N. Lisetski, Olga V. Vashchenko, Natalia A. Kasian, and Alina O. Krasnikova*

6.1 Introduction 164
6.2 Lipid Bilayer as the Structural-Functional Base of Cell Membranes 165

6.3 Effects of Non-Lipid Components on the Phase State of Model Phospholipid Membranes 169
6.3.1 General Considerations 169
6.3.2 MTA of Protein Nature 172
6.3.3 Cholesterol and Other Steroids 173
6.3.4 Provitamin D 174
6.3.5 Urocanic Acid 174
6.4 Effects of Ion Medium on Liquid Crystal Phase Transitions of Phospholipid Membranes 175
6.5 Testing of the Joint Action of Drugs by Their Effects on Model Phospholipid Membranes 182
6.6 Conclusions 187

**7. Interactions of Biologically Active Redox-Sensitive Dyes with Nanomaterials: Mass Spectrometric Diagnostics 193**

*Marina V. Kosevich, Oleg A. Boryak, Vitaliy V. Chagovets, Vadim S. Shelkovsky, and Valerij A. Pokrovskiy*

7.1 Introduction 194
7.2 Harnessing of Redox Properties of Dyes in Functioning of Nanomaterials and Nanodevices 195
7.3 Redox-Active Dyes 196
7.4 Mass Spectrometry in Studies of Nanomaterials 197
7.5 Observation of Reduction Reactions of Dyes under Mass Spectrometric Conditions 197
7.6 Reduction of Imidazophenzine Dyes under Mass Spectrometric Conditions 200
7.7 Interactions of Imidazophenazine Dyes Derivatives with Nanostructured Surfaces 204
7.7.1 Positive Ion Mass Spectra 205
7.7.2 Negative Ion Mass Spectra 207
7.7.3 Contribution of Field Ionization Mechanism to the LDI from the Nanostructured Graphite Surface 209
7.7.4 Intermolecular Interactions in a Nanocomposite of Methylene Blue Dye with Carbon Nanotubes 212

7.7.5 Interactions of Methylene Blue Dye with Mesoporous Oxide Films 219
7.7.6 Interactions of Methylene Blue with Modified Silicon Surface 221
7.8 Incorporation of Dyes into Surface Nanolayers 222
7.9 Conclusions 223

**8. Nanosized Complexes of Bioorganic Molecules in Low-Temperature Matrices 235**

*Alexander M. Plokhotnichenko and Victor A. Karachevtsev*

8.1 Introduction 236
8.2 Matrix Isolation Method: Opportunities and Limitations 238
8.2.1 Some Experimental Details to Study Molecular Complexes by Matrix Isolation Method 242
8.2.2 Interpretation of Spectral Data 246
8.3 The Formation of Molecular Complexes in Matrix 247
8.3.1 H-Bonded Complexes of Phenols 249
8.3.2 $\pi$–$\pi$ Stacking Complexes of Flat Heterocyclic Molecules in the Low Temperature Matrices of Inert Gases 254
8.4 Conclusions 260

**9. Kinetics Framework for Nanoscale Description of Environment-Induced Transition Processes in Biomolecular Structures 267**

*Elmar Petrov and Victor Teslenko*

9.1 Introduction 268
9.2 Master Equation for Averaged Populations 275
9.2.1 Stochastic Hamiltonian and Stochastic Equation for State Populations 276
9.2.2 Stochastically Averaged Master Equation 278
9.3 Transition Rate Constants 280
9.3.1 Temperature-Independence of Desensitization Onset of $P2X_3$ Receptors 281

9.3.2 Temperature-Independent Degradation of Endogenous Protein PER2 282
9.4 Fractional Cooperativity of Biomolecular Structures 283
9.5 Conclusions 286

**10. Polymer-Mediated Interactions between Nanoparticles and Their Effect on the Coagulation-Fragmentation in Polymer Composites 293**

*Alexander I. Chervanyov*

10.1 Introduction 294
10.2 Self-Consistent Field Theory of Polymer-Mediated Interactions 299
10.2.1 Self-Consistent Mean Field Theory as Applied to the Study of Polymer-Mediated Interactions 299
10.2.2 Mathematical Development of Polymer SCMFT 302
10.2.3 Potential Theory of Polymer-Mediated Interactions: Way of Solving SCMFT Equations 305
10.2.4 Effective Potential of the Interactions between Nanocolloids Mediated by Irreversibly Adsorbed Polymers 309
10.3 Effect of the Polymer-Mediated Interactions on the Rates of Colloid Coagulation in the Presence of Adsorbing and Non-Adsorbing Polymers 311
10.4 Effect of Polymer-Mediated Interactions on the Stability of Filler Agglomerates in Rubbers 313
10.5 Conclusions 318

**11. Point-Contact Sensors and Their Medical Applications for Breath Analysis: A Review 327**

*Gennadii V. Kamarchuk, Alexander P. Pospelov, Lyudmila V. Kamarchuk, and Ievgeniia G. Kushch*

11.1 Introduction 328
11.2 Fundamentals of the Point-Contact Sensor Development 331

11.2.1 Yanson Point-Contact Spectroscopy 331
11.2.2 Point-Contact Gas-Sensitive Effect 336
11.3 Methods for Producing Point-Contact Sensors 344
11.3.1 Chubov Displacement Technique 344
11.3.2 Method of Twisting Metal Wires 346
11.3.3 Dendrite Point Contacts 348
11.4 A New Approach to Sensor Analysis of Exhaled Breath Based on the Point-Contact Gas-Sensitive Effect 351
11.5 Development of Methods of Noninvasive Diagnosis by Point-Contact Sensors 357
11.6 Conclusions 367

**12. Nanophotonic Sensor for Polycyclic Aromatic Hydrocarbon Detection 381**

*Olga A. Sushko and Mykola M. Rozhitskii*

12.1 Introduction 382
12.2 Chemical Carcinogenesis and Metabolism of Benzo[a]pyrene 382
12.3 Analytical Methods of Benzpyrene Detection 385
12.4 Physico-Chemical Properties of Semiconductor Quantum Dots as Detector Elements 387
12.5 The Basics of Physical Processes in a Nanophotonic Sensor during Assay 393
12.6 Quantum-Chemical Calculation of Benzo[a]pyrene Electronic Parameters and Optimal Size of the Emitting Spherical Semiconductor Quantum Dot's Nucleus Determination 397
12.7 Electrochemical Investigation of Semiconductor Quantum Dots 400
12.8 Spectral Investigation of Benzo[a]pyrene Solution and Colloidal Semiconductor Quantum Dots 401
12.9 The Method of Sensor's Working Electrode Modification 402
12.10 Nanophotonic Sensor for Polycyclic Aromatic Hydrocarbon Detection 403

12.11 Nanophotonic Sensor for Polycyclic Aromatic Hydrocarbons Detection Testing on Model Solutions 404

*Index* 411