

**Annual Review of Physical Chemistry, 2007.** S. R. Leone *et al.* (eds). Annual Reviews Inc, 4139 El Camino Way, P.O. Box 10139, Palo Alto, California 94303-0139, USA. Vol. 58. 758 pp.

When chemistry departments and chemists worldwide are embracing biology and/or materials science, it is not surprising that the editors and authors of the *Annual Review of Physical Chemistry* have come out with a colourful issue in which at least half the articles fall in the subset of physical chemistry of biological molecules or materials. Although the general format laid out for the *Annual Review of Physical Chemistry* years ago has been maintained in this issue (it starts with the self-narrated career portrait of a distinguished physical chemist), the topics covered in this issue are relevant in today's physical chemistry and physical chemists must remain updated with the changing definition of physical chemistry and recent developments in the area.

This volume begins with the chapter in which Bradley Moore, starting in the year 1960, traverses his entire research career in chemical physics at Berkeley. Moore's narration of how the early excitement with his 'first spectroscopic observation' of shooting stars while lying flat on a hay wagon, when growing up in a small farm town in Pennsylvania, led to his becoming a physical chemist is absorbing. He then describes his studies of energy transfer in various electronically, vibrationally, and chemically excited molecular systems. He enters into his favourite field within the gas-phase chemical dynamics, namely unimolecular and bimolecular reactions, where he has looked at the rovibrational energy transfers in the excited state of a polyatomic molecule for more than two decades. In fact, he has spent more than a decade investigating various aspects of the unimolecular dissociation dynamics of formaldehyde and its variants. Moore finishes the chapter with an epilogue where his deep sense of loyalty to his thesis supervisor George Pimental, reminds the reader about how objective thesis supervisors like Pimental, who recommends a student who never achieved the primary goal in research that was set out in the beginning, for the best academic job in the country, are fast disappearing from the world! This chapter is refreshing as well as inspiring for the young

physical chemists/chemical physicists who are to begin a career in the subject.

All the other articles can be grouped into various subfields of physical chemistry. Physical chemistry/chemical physics and spectroscopy at an interface or at the solid state have been described in at least eight articles. In a lucid and well-written article, Willets and Van Duyne have described surface plasmon resonance-based spectroscopic techniques for sensing application. Techniques based on localized surface plasmon resonance (LSPR) such as chronocoulometry and surface enhanced Raman scattering (SERS) have been described in detail, explaining how the LSPR spectral band position shifts depending on the size and shape of the nanoparticle, or how the enhancement factor of surface-enhanced resonance Raman scattering is a product of the nonresonant SERS enhancement of the substrate and the resonance Raman spectrum of the adsorbate. Johannes Barth deals with molecular architectonic on metal surface in an article and demonstrates that it is possible to steer and monitor the assembly of molecular nanoarchitecture in detail. Scanning tunneling microscopy has opened up new atomistic insight into self-assembly of organic clusters, chains and superlattices, which offers enormous potential for nanodevice formulation. Single-molecule spectroscopy of adsorption and diffusion on an analyte on silica surfaces has provided information on peak broadening and asymmetry in chromatograms of drug molecules, peptides and proteins. This has been illustrated in an article with examples from the current literature by Wirth and Legg. A few atom noble metal quantum dots which are highly fluorescent and water-soluble and behave as artificial atoms with discrete electronic transitions that are tunable over the visible-near infrared region, have been reviewed by Zheng *et al.* Their absorption and emission spectra, size-correlation with emission spectra, and photophysical properties have been determined by single-molecule microscopy and have been elaborated in the article. Exciton photo-physics and the importance of excitons to single-walled carbon nanotube optics have been presented in an article by Dresselhaus *et al.*, while multiexciton effects on photoluminescence and other spectral and dynamical properties in semiconductor nanocrystals have been discussed in detail in a separate article by Klimov.

Measurement of single-molecule conductance using scanning probe techniques has been reviewed by Chen *et al.*

Another eight articles which have been included in this issue may be grouped under chemical physics/physics of biological systems. This also shows the noticeable change in the perception of what physical chemistry is today, in spite of the fact that the *Annual Review of Biophysics and Biomolecular Structure* is published yearly and could contain any or all of these articles! For example, the article by Millhauser on ESR spectroscopy of Cu(II) binding of the octarepeat domain in the prion protein PrP<sup>C</sup>, could certainly qualify more to appear in the latter than in this volume.

Investigation on the motion of a polymer at liquid-liquid or solid-solid interfaces studied by time-resolved techniques throws light on the diffusion coefficient of the polymer and can provide insights into molecular understanding of lubrication. This has been presented in an article by Bae and Granick. In a more sophisticated approach to study the structure and dynamics of conjugated polymers in anisotropic solvents, Barbara *et al.* have combined single-molecule spectroscopy and molecular dynamics (MD) simulation in an article. Mass spectrometry which has become an invaluable tool in studying analytical chemistry of biologically important molecules and processes over the past 15 years or so, following the commercialization of the electrospray and laser desorption ionization mass spectrometers, has been covered by Wyttenbach and Bowers. They have presented how intermolecular interactions such as protein-protein, nucleic acid-nucleic acid, solvent-protein, etc. can be examined by various types of mass spectrometry. The underlying structure and organization (topography) of biological membranes in micrometre length scale has been probed by fluorescence topography imaging and presented in an article by Groves.

Gas and condensed phase dynamics and spectroscopy have been discussed in six articles. Very sophisticated femtosecond stimulated Raman spectroscopy (FSRS) that provides vibrational structural information with high temporal and spectral resolution has been described by Kukura *et al.* The FSRS technique proposed by the same group in 2005, where structural evolution of the primary isomerization in  $\beta$ -carotene in vision was

mapped following the initial excitation, offers, in principle, tremendous scope for gaining insights into a large variety of chemical and biochemical reactions in the ultrafast timescale. Development of the technique further to cover a wide range of wavelengths for the stimulated Raman process and multidimensional implementation to study vibrational coherence and coupling provide an exciting future for the FSRS technique. State-to-state dynamics of elementary biomolecular reactions has been described by Yang, and spectroscopy of amino acids and nucleic acid bases has been presented by de Vries and Hobza. Duncan and Prezhdo describe recent developments in explicit time-dependent modelling of photo-induced charge separation in dye-sensitized semiconductor solar cells. The results are of importance in a variety of applications that would involve molecular electronics, analytical detection, quantum confinement devices, etc. The other review by Levine and Martinez, is on photoisomerization, the fundamental process in vision and in other processes that convert light energy into mechanical motion. Cis-trans photoisomerization about the C=C bond through conical intersection has been relooked theoretically beyond one dimension. In an interesting article aging of organic aerosols has been dealt with, where difficulties of comparing laboratory data with field measurements have been highlighted. Since climate and human health in a global scale is of prime concern today, this article by Rudich *et al.* brings out the necessity of developing an understanding of complex atmospheric chemistry/processes and their kinetics through laboratory experiments.

Two of the major topics of research in physical chemistry that have been around for quite sometime are protein folding and glass transition, both of which are discussed in this issue. Scheraga *et al.* consider the methods of folding a protein *in silico*. The area is in a state of rapid development with the introduction of new techniques, which makes it possible to study folding pathways from completely unfolded structures. The review presents algorithms for MD, and their extensions and applications to protein-folding studies using all-atom models with explicit and implicit solvent as well as reduced models of polypeptide chains. Random first-order transition theory of the glass transition is reviewed by Lubchenko and Wolynes. The authors em-

phasize the experimental tests of the theory and show that theory goes a long way in predicting/explaining many of the distinct phenomena associated with the transition.

Understanding complex fluids on a theoretical level is the subject of two articles. Balazs describes in detail the use of a variety of computational techniques to investigate how the self-assembly of complex mixtures can be guided by surfaces or external stimuli to form spatially regular or temporally periodic patterns. She shows how thermodynamic and hydrodynamic effects can be exploited to create regular arrays of nanowires or monodisperse, particle-filled droplets. Density functional theory is used to describe microscopic structures and phase behaviour of soft, condensed matter in the article by Wu and Li. After describing the different strategies used to formulate the free-energy functional of complex fluids, the article describes recent advances in understanding the dynamic properties of complex fluids and kinetics of phase transitions.

Cellular systems in biology, where the small molecular populations of only a few reactant species can lead to deviations from the predictions of deterministic differential equations of classical chemical kinetics have interesting internal dynamics. Gillespie reviews the theory of stochastic chemical kinetics and discusses recent advances in methods for using the theory to make numerical simulations. Qian describes statistical thermodynamics of far-from-equilibrium systems, with applications to cells and biochemical systems. He points out that the currently available models quantitatively describe energetics and thermodynamics in phosphorylation-dephosphorylation switches, GTPase timers, and specificity amplification through kinetic proofreading. Theorists' perspectives on molecular motors are presented by Kolomeisky and Fisher. Aspects of motor-protein dynamics, helpful in understanding single-molecule experiments involving biomechanical properties of such motors are presented. The field has been rapidly developing and much more is expected to happen in the area. Nanomechanical properties form the subject of an article by Mielke *et al.* who describe fracture mechanics at the nanoscale. They summarize the experimental efforts to measure fracture strengths of inorganic and carbon nanotubes, and then go

on to describe the attempts to understand the measurements in terms of theory.

Although we believe that this particular issue has too many articles addressing advancements in materials science and biological chemistry, some of them are well written and provide a broad perspective of the field, while others are limited and narrow in scope. However, they all provide recent references in the field and present the background for further reading on the subject. This volume of the *Annual Review of Physical Chemistry* is certainly recommended to all libraries.

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Reading this large volume was illuminating. Twenty years ago, picking up a volume of an *Annual Review* was a must before one started working on a problem, since the information provided in a single chapter covered almost all aspects of the area of interest. What is striking now is how specific some chapter topics are, detailing a single well-defined issue. This is clearly an indication of the huge explosion in knowledge over the last two decades in specific areas, prohibiting a more broad-based coverage. Therefore, in this volume we see chapters on the allosteric regulation of G-protein coupled receptors (GPCRs), constitutive activation of GPCRs, and the use of retinoids in eye disease, along with more general topics on AMP-activated protein kinase, cell signalling and neuronal death, and the effects of estrogen on neuronal physiology.

No treatise on pharmacology and toxicology can be found without discussions on GPCRs, since the maximum number of therapeutics in the market are directed to various members of this extraordinarily large family of proteins. It is therefore pleasing to see two chapters that deal with features of GPCRs that are impor-