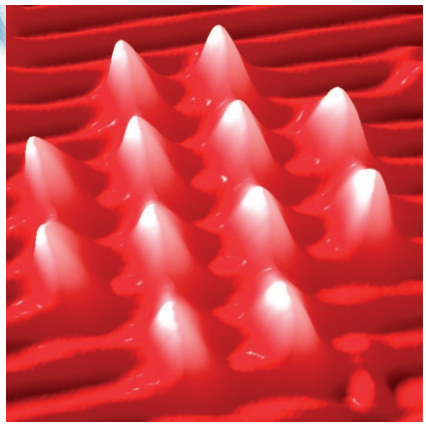
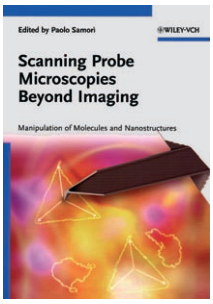


Scanning Probe Microscopies Beyond Imaging



Manipulation of Molecules and Nanostructures. Edited by *Paolo Samori*. Wiley-VCH, Weinheim 2006. 546 pp., hardcover € 149.00.—ISBN 3-527-31269-2

The 25th anniversary of the invention of the scanning tunneling microscope by Binning and Rohrer was celebrated last year. This technique revolutionized our understanding of the structure of surfaces and of processes such as molecular adsorption and crystal growth, as it gave imaging with atomic resolution. It took less than a decade for scanning tuneling microscopy (STM) to emerge from the vacuum into the liquid state, so that one could, for example, study electrochemistry at electrode surfaces. Soon STM was used to manipulate (or even write with) single atoms, and to investigate electrical properties and vibrations of single molecules. Moreover, human intervention on the nanoscale became possible. Nowadays, STM enables us to use electrons to induce chemical reactions in single molecules, as well as to construct artificial molecular assemblies (see Figure showing a Swiss Cross assembled from twelve propene molecules on a copper surface; M. Parschau, Empa). The atomic force microscope was invented by Binning, Quate, and Gerber only five years after the scanning tuneling microscope, and has an even greater impact in science today. These two techniques gave birth to nanotechnology, and will be of paramount importance in the future for new emerging fields of nanoscience.

The book *Scanning Probe Microscopies Beyond Imaging* covers the latest developments in the field of scanning probe microscopy (SPM). It gives a broad overview of different applications of SPM beyond imaging, in particular those that exploit STM- and AFM-based approaches for soft materials. The 16 chapters have been written by 40 experts who are actively working in the field. The book is structured under four main topics: "Scanning Tunneling Microscopy-Based Approaches" (four chapters), "Scanning Force Microscopy-Based Approaches" (nine chapters), "Other SPM Methodologies" (one chapter), and "Theoretical Approaches" (two chapters). The AFM part is further divided into the fields "Patterning" (two chapters), "Mechanical Properties" (three chapters), "Bond Strength and Tracking Chemical Reactions" (two chapters), and "Electrical Properties of Nanoscale Objects" (two chapters).

The first chapter surprisingly deviates right away from the main topic of the book; it deals with self-assembled chiral monolayers imaged by STM. No manipulation is involved. However, it demonstrates that STM is an extremely powerful method for investigating the formation of two-dimensional molecular patterns. In particular, surface chirality is a very important and popular topic in surface science today, with applications to chiral recognition in two dimensions, optical resolution of enantiomers by crystallization, novel photonic materials, and enantioselective heterogeneous catalysis.

Chapter 2 deals with STM at the solid/liquid interface, including scanning tunneling spectroscopy (STS) on single molecules. Whereas Chapter 2 focuses on single-molecular electronic phenomena, Chapter 3 describes how STM can be used to reposition atoms and molecules or to manipulate large molecules. The last STM chapter describes how STM can be used as a spectroscopic tool and to acquire vibrational spectra of single molecules by inelastic electron tunneling.

The AFM part starts with nanolithography, which includes patterning of organic nanostructures and dip-pen nanolithography. Both techniques can be used for chemical and biological patterning on the nanometer scale, and may play an important role in the future development of nanosensors. Applications of AFM for studying the morphology of polymers and other macromolecular systems are also described. The techniques of pulsed-force-mode scanning force microscopy (Chapter 8) and force spectroscopy (Chapter 9) can be used to study the interaction between the tip and the sample in detail, and to measure forces between AFM probes and surfaces. Two chapters are devoted to AFM-probe chemistry and chemical force microscopy. Besides chemical analysis by the use of functionalized tips, the reader learns that AFM can be used to measure the forces needed to unfold macromolecules and to rupture chemical bonds. One chapter shows how electrical conductance of nanoscale systems, such as nanotubes and molecular wires, can be determined by the use of metalized AFM probes, and two chapters give introductions to Kelvin-probe force microscopy and scanning electrochemical microscopy. The last two chapters are devoted to theoretical approaches towards describing elastic and inelastic tunneling and the mechanical properties of single molecules.

Overall, this book gives an excellent overview of SPM beyond imaging. The working principles of new methodological approaches are well introduced, and many experimental examples help the reader to quickly assess the capabilities of all the techniques. The table of contents and the index are well prepared. Layout and design are excellent, although a few of the figures have very

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poor resolution. Two important techniques, electric and magnetic force microscopies (EFM, MFM), are unfortunately not included. Nevertheless, the book can be recommended as a reference source for scientists as well as a textbook for advanced students. For the specialist it is a valuable source of information.

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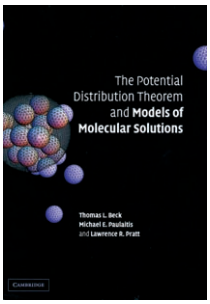
DOI: 10.1002/anie.200685466

The Potential Distribution Theorem and Models of Molecular Solutions



By *Thomas L. Beck*, *Michael E. Paulaitis* and *Lawrence R. Pratt*. Cambridge University Press, Cambridge 2006. 230 pp., hardcover £ 65.00.—ISBN 0-521-82215-7

To write a book about molecular theory is a real challenge. Theories of molecular liquids have never been simple. Most of the attempts at writing such books have led to opinions like that expressed in the first English edition of the influential textbook *Statistical Physics*, by Landau and Lifshitz, in 1969: "We have not included in this book the various theories of ordinary liquids and of strong solutions, which to us appear neither convincing nor useful". Such a statement underlines the limitations of available theories of liquids at that time. Thus, it is very pleasing that Thomas L. Beck, Michael E. Paulaitis, and Lawrence R. Pratt have taken on this challenge by presenting a book entitled *The Potential Distribution Theorem and Models of Molecular Solutions*. All three authors are well-known experts in the fields of quantum simulation methods, phase theory of solutions, and related modeling, as well as the molecular thermodynamics of hydration. In the introduction to this nice book, the authors reassure us that practical molecular theory can be simpler than a first impression suggests.

The authors decided to emphasize those aspects of the theory of molecular liquids that are different from the familiar theory of atomic liquids. One reason is that the theory of simple liquids is well described elsewhere. The other reason is that especially the molecular aspects of solutions are essential to topics of current interest such as ion channels.

The book is clearly structured in eight chapters. The first chapter gives a historical sketch of efforts in the last few decades to describe liquid and solution properties. Different approaches have been used to characterize simple (atomic) liquids, molecular liquids, and complex liquids. The authors emphasize that theories of molecular liquids require molecule-specific features, which the theory of simple liquids does not provide. In that sense, molecular liquid water is recognized to be a particularly complex molecular liquid. The second chapter shows that an understanding of statistical thermodynamics is fundamental to the appreciation of molecular solutions. Here the reader will not find anything new beyond the contents of well-known textbooks on thermodynamics and statistical mechanics. However, the knowledge of how free energies and chemical potentials can be calculated from the partition function will be needed to understand the central theorem of the book, which is stated in Chapter 3. The potential distribution theorem (PDT), which was developed by Widom in 1963, and is sometimes called Widom's particle insertion formula, is the central organizing principle in the theory and in the realistic modeling of molecular solutions. The authors offer a couple of reasons why the potential distribution theorem has not been widely accepted. However, they show that the theorem gives some vital theoretical insights into molecular modeling, as approached either through computer simulations or by purely theoretical methods in general. They point out that this theorem has recently stimulated a new stage of development in the molecular modeling of solutions, namely: quasi-chemical theories that promise accurate molecular and chemical detail on the basis of available electronic structure computational methods of molecular science. The authors see PDT as directly analogous to the partition function, which expresses the Gibbsian ensemble formulation of statistical mechanics. PDT can be regarded as a formula for a thermodynamic potential in terms of a partition function. However, in contrast to Gibbsian partition functions, the PDT is built upon a local view of thermodynamics and depends on local information.

The authors have made an effort to simplify this complex subject, with down-to-earth presentations of molecular theory. The chapters about PDT and models of molecular solutions lead to the heart of the book, which is the idea of a quasi-chemical theory (Chapter 7), followed in Chapter 8 by its application to particular examples, such as hydrophobic effects and hydrophilic phenomena.

The authors discuss the subject in a concise and simple manner, and illustrate the text with useful models of solution thermodynamics and numerous exercises. Modern quasi-chemical theories that permit statistical thermodynamic properties to be studied on the basis of electronic structure calculations are developed at length, and the theoretical results are tested by comparing them with ab initio molecular dynamics simulations.

This book presents a fresh view on old problems and on recent intensive studies. It is suitable for students with a strong background in a physical science, and especially for graduate students embarking on research activities in molecular modeling of solutions in chemistry, chemical engineering, biophysics, molecular biotechnology, and nanotechnology. This beautiful book belongs in every physics and chemistry library.

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