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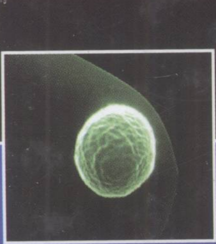
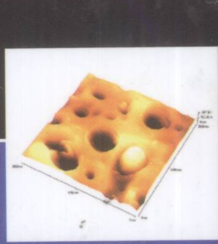
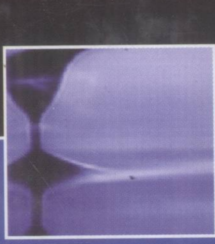
ATOMIC FORCE MICROSCOPY IN PROCESS ENGINEERING


An Introduction to AFM for Improved Processes and Products

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ATOMIC FORCE MICROSCOPY IN PROCESS ENGINEERING

INTRODUCTION TO AFM FOR IMPROVED PROCESSES AND PRODUCTS

W. Richard Bowen and Nidal Hilal

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INTRODUCTION TO AFM FOR IMPROVED PROCESSES AND PRODUCTS

Preface

Atomic force microscopy (AFM) was first described in the scientific literature in 1986. It arose as a development of scanning tunnelling microscopy (STM). However, whereas STM is only capable of imaging conductive samples in vacuum, AFM has the capability of imaging surfaces at high resolution in both air and liquids. As these correspond to the conditions under which virtually all surfaces exist in the real world, this greatly increased the potentially useful role of scanning probe microscopies. This great potential of AFM led to its very rapid development. By the early 1990s, it was moving outside of specialist physics laboratories and the first commercial instruments were becoming available.

At the time, our main process engineering research activities were in the fields of membrane separation processes and colloid processing. Both of these fields involve the manipulation of materials on the micrometre to the nanometre length scales. To image the materials used in such processes, we used scanning electron microscopy, which was expensive, time-consuming, and even more undesirably usually involved complex sample preparation procedures and measurement in vacuum which could result in undesirable experimental artefacts. Our imagination was fired and our research greatly facilitated, following an inspiring lecture given by Jacob Israelachvili at the 7th International Conference on Surface and Colloid Science in Compiègne, France, in July 1991, in which he described some of the very first applications of AFM in colloid science. Our first grant application for AFM equipment was written very shortly afterwards!

Since that time there has been an enormous development of the capabilities and applicability of AFM. Physicists have devised a bewildering range of experimental techniques for probing the different properties of surfaces. Scientists, especially those working in the biological sciences, have been able to make remarkable discoveries using AFM that would have been otherwise unobtainable. A huge amount of scientific literature has appeared including a number of introductory and advanced books. However, despite the achievements and great potential for the application of AFM to process engineering, there is no book-length text describing such achievements and applications. Further, the specialist nature of the primary literature and the disciplinary strangeness of the existing book-length texts can appear rather formidable to engineers who might wish to apply AFM in their work. Hence, it is our assessment that the benefit of AFM to the development of process engineering is under-fulfilled. Nevertheless, the significant decrease in cost of commercial AFM equipment, and its increasing 'user-friendliness', has made the technique readily accessible to most engineers. We were, therefore, motivated to put together the present text with the specific intention of describing the achievements and possibilities of AFM in a way which is directly relevant to the work of our process engineering colleagues, with the hope that we will inspire them to apply this remarkable technique for the benefit of their own activities.

We begin in Chapter 1 by providing an outline of the basic principles of AFM. The chapter introduces the main features of AFM equipment and describes the imaging modes which are most likely to be of benefit in process engineering applications. Such knowledge of the main operating modes should allow the reader to interpret the nature of the many subtle variations described in the primary research literature. We also introduce a remarkable benefit of AFM equipment, because it is a *force* microscope it can be used to directly measure surface interactions with very high resolution in both force and distance. An especially useful application of this capability is the use of 'colloid probes', the nature of which is introduced and the benefits of which become apparent in several of the later chapters.

AFM can generate beautiful images of surfaces at subnanometre resolution. However, the detailed interpretation of the features of such images can benefit greatly from an understanding of the fundamental interactions from which they arise. This is the subject of Chapter 2. Depending on the materials being investigated and the experimental conditions, the interactions which give rise to such images, either separately or simultaneously, include van der Waals forces, electrical double layer forces, hydrophobic interactions, solvation forces, steric interactions, hydrodynamic drag forces and adhesion. AFM also has the capability to quantify such interactions, especially using colloid probe techniques. For this reason, mathematical descriptions of such interactions are given in forms which have proved of practical use in process engineering.

Once the basics of AFM have been outlined, it is possible to move to a description of specific applications. Process engineering is a diverse and growing field comprising both established processes of great societal significance and new areas of huge promise. We begin in Chapter 3 by describing investigations of an established and important type of phenomenon – the quantification of particle–bubble interactions. Such interactions are of fundamental significance in some of the largest-scale industrial processes, most notably in mineral processing and in wastewater treatment. It is especially the capability of AFM equipment to quantify the interactions between bubbles and micrometre size particles that can lead to the development of processes of increased flotation efficiency and greater specificity of separation. This is a remarkable example of how nanoscale interactions control the efficiency of megascale processes.

Membrane separation processes are one of the most significant developments in process engineering in recent times. They now find widespread application in fields as diverse as water treatment, pharmaceutical processing, food processing, biotechnology, sensors and batteries. Membranes are most usually thin polymeric sheets, having pores in the range from the micrometre to subnanometre, that act as advanced filtration materials. Their separation capabilities are due to steric effects and the whole range of interactions that can be probed by AFM. Hence, there is a very close match between the factors that control the effectiveness of a membrane process and the measurement capabilities of AFM. In Chapter 4, we provide a survey of the numerous ways in which AFM can be used to study the factors controlling membrane processes. We consider both advanced imaging and force measurement techniques, and how they may be combined, for example, to provide a 'visualisation' of the rejection of a colloid particle by a membrane pore. Chapter 5 is more especially concerned with the use of AFM in the development of new membranes with specifically desirable properties. We focus, in particular, on the development of fouling resistant membranes, i.e. membranes with the minimum of unwanted adhesion of substances from the fluids being processed.

In the pharmaceutical industry, there is an increasing drive to develop new ways of drug delivery, both means for the presentation of drugs to the patient and of drug formulations which target specific sites in the body. Both of these goals can benefit from knowledge of structures and interactions at the nanoscale. Thus, pharmaceutical development can benefit from both the imaging and force measurement capabilities of AFM, as described in Chapter 6. The colloid probe, or more precisely drug particle probe, techniques are again very important in this work. However, there is also scope for the use of advanced techniques, such as micro- and nanothermal characterisation using a scanning thermal microscope (SThM), which can provide spatial information at a resolution unavailable to conventional calorimetry.

Bioprocessing is acquiring a sophistication that was unimaginable even a few years ago. An important example is given in Chapter 7. Cells sense and respond to their surrounding microenvironment. The chapter reviews the application of micro/nanoengineering and AFM to the investigation of cell response in engineered microenvironments that mimic the natural extracellular matrix. In particular, the chapter reports the use of micro/nanoengineering to make structures that aid the understanding of fundamental cellular interactions, which in turn help further development of new therapeutic methods. Specific attention is given to the combination of AFM with optical microscopy for the simultaneous interrogation of biophysical and biochemical cellular processes and properties, as well as the quantification of cell viscoelasticity.

Throughout the process industries, and more generally in manufacturing, the surfaces of materials are modified with coatings to protect them from hostile conditions and to functionalise them for a variety of purposes. In particular, ultrathin coatings play a crucial role in many processes, ranging from protection against chemical corrosion to microfabrication for microelectronics and biomedical devices. Chapter 8 describes the use of AFM for the study of the fine structure and local nanomechanical properties of such advanced polymer monolayers and submonolayers. AFM allows the real-time/real-space monitoring of relevant physicochemical surface processes. As miniaturisation of electronic and medical devices approaches the nanometre scale, AFM is becoming the most important characterisation tool of their nanostructural and nanomechanical properties.

AFM has been considered primarily as a technique for the investigation of the surfaces of solid materials, with the considerable benefit that it can be used to carry out such investigations in liquid environments. However, AFM may also be used to study the properties of such liquids themselves. This is the topic of Chapter 9, which describes dynamic studies of confined fluids, micro- and nanorheology, cavitation and adhesive failure in thin films, and meso-scale experimental studies of the tensile behaviour of thin fluid films. Such studies benefit considerably from the coupling of AFM with high-magnification optical microscopy and high-speed video techniques. The development of such studies may be of considerable importance for the many large-scale processes that depend on the properties of thin liquid films, and also for instances where the available quantities of fluids are tiny, such as for synovial fluid.

In the final chapter, we have pooled the thoughts of the contributors to provide a vision of some of the ways in which AFM may contribute to the development of process engineering in the future.

We thank all of the authors who have collaborated in the writing of this volume. We are very grateful for their willingness to devote time to this task and for their timely delivery of high-quality manuscripts. We also thank the many colleagues and research students who have contributed to the work described. Particular thanks are due to Dr Peter M. Williams. Peter worked as a research technician at our centre when we first started AFM studies. The results of our research as presented in this volume owe much to his technical ingenuity and patience.

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February 2009

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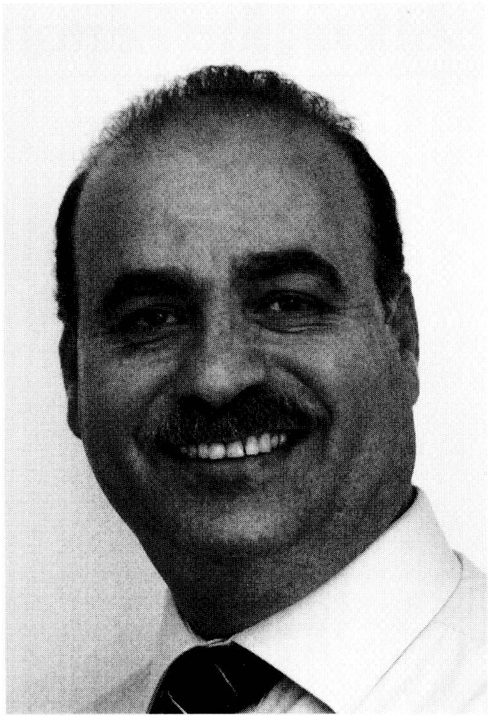

Professor Nidal Hilal is a Fellow of the Institution of Chemical Engineers and currently the Director of the Centre for Clean Water Technologies at the University of Nottingham. He obtained a PhD in Chemical Engineering from the University of Wales in 1988. Over the years, he has made a major contribution becoming an internationally leading expert in the application of Atomic Force Microscopy in process engineering and membrane technology. Professor Hilal is the author of over 300 refereed publications, including 4 textbooks and 11 invited chapters in international handbooks. In recognition of his substantial and sustained contribution to scientific knowledge, he was awarded a senior doctorate, Doctor of Science (DSc), from the University of Wales and the Kuwait Prize for Water Resources Development in 2005. He is a member of the editorial boards for a number of international journals and an advisor for international organizations including the Lifeboat Foundation. He is also on the panel of referees for the UK and international Research Councils.

Professor Hilal acknowledges His Majesty King Abdullah Bin Abdul Aziz Al-Saud of Saudi Arabia, who is a keen advocate for nanotechnology and process engineering, particularly in the field of desalination and water research for the benefit of all humanity.

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CHAPTER

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1.1 INTRODUCTION

The atomic force microscope (AFM), also referred to as the scanning force microscope (SFM), is part of a larger family of instruments termed the scanning probe microscopes (SPMs). These also include the scanning tunnelling microscope (STM) and scanning near field optical microscope (SNOM), amongst others. The common factor in all SPM techniques is the use of a very sharp probe, which is scanned across a surface of interest, with the interactions between the probe and the surface being used to produce a very high resolution image of the sample, potentially to the sub-nanometre scale, depending upon the technique and sharpness of the probe tip. In the case of the AFM the probe is a stylus which interacts directly with the surface, probing the repulsive and attractive forces which exist between the probe and the sample surface to produce a high-resolution three-dimensional topographic image of the surface.

The AFM was first described by [1]Binnig *et al.* as a new technique for imaging the topography of surfaces to a high resolution. It was created as a solution to the limitations of the STM, which was able to image only conductive samples in vacuum. Since then the AFM has enjoyed an increasingly ubiquitous role in the study of surface science, as both an imaging and surface characterisation technique, and also as a means of probing interaction forces between surfaces or molecules of interest by the application of force to these systems. The AFM has a number of advantages over electron microscope techniques, primarily its versatility in being able to take measurements in air or fluid environments rather than in high vacuum, which allows the imaging of polymeric and biological samples in their native state. In addition, it is highly adaptable with probes being able to be chemically functionalised to allow quantitative measurement of interactions between many different types of materials – a technique often referred to as chemical force microscopy.

At the core of an AFM instrument is a sharp probe mounted near to the end of a flexible microcantilever arm. By raster-scanning this probe across a surface of interest and simultaneously monitoring the deflection of this arm as it meets the topographic features present on the surface, a three-dimensional picture can be built up of the surface of the sample to a high resolution. Many different variations of this basic technique are currently used to image surfaces using the AFM, depending upon the properties of the sample and the information to be extracted from it. These variations include 'static' techniques such as contact mode, where the probe remains in constant contact with the sample, and 'dynamic' modes, where the cantilever may be oscillated, such as with the intermittent or non-contact modes. The forces of interaction between the probe and the sample may also be measured as a function of distance by the