

# Nano-Surface Chemistry



edited by  
**Morton Rosoff**

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**Morton Rosoff**  
*Long Island University*  
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# **Nano-Surface Chemistry**

## Preface

Tools shape how we think; when the only tool you have is an axe, everything resembles a tree or a log. The rapid advances in instrumentation in the last decade, which allow us to measure and manipulate individual molecules and structures on the nanoscale, have caused a paradigm shift in the way we view molecular behavior and surfaces. The microscopic details underlying interfacial phenomena have customarily been inferred from in situ measurements of macroscopic quantities. Now we can see and “finger” physical and chemical processes at interfaces.

The reviews collected in this book convey some of the themes recurrent in nano-colloid science: self-assembly, construction of supramolecular architecture, nanoconfinement and compartmentalization, measurement and control of interfacial forces, novel synthetic materials, and computer simulation. They also reveal the interaction of a spectrum of disciplines in which physics, chemistry, biology, and materials science intersect. Not only is the vast range of industrial and technological applications depicted, but it is also shown how this new way of thinking has generated exciting developments in fundamental science. Some of the chapters also skirt the frontiers, where there are still unanswered questions.

The book should be of value to scientific readers who wish to become acquainted with the field as well as to experienced researchers in the many areas, both basic and technological, of nanoscience.

The lengthy maturation of a multiauthored book of this nature is subject to life’s contingencies. Hopefully, its structure is sound and has survived the bumps of “outrageous fortune.” I wish to thank all the contributors for their courage in writing. It is their work and commitment that have made this book possible.

*Morton Rosoff*

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# Introduction

The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level is ultimately developed—a development which I think can’t be avoided.

Richard Feynman

God created all matter—but the surfaces are the work of the Devil.  
Wolfgang Pauli

The prefix *nano-*, derived from the Greek word meaning “dwarf,” has been applied most often to systems whose functions and characteristics are determined by their tiny size. Structures less than 100 nanometers in length (i.e., one-ten-millionth of a meter) are typical in nano-technology, which emphasizes the approach of building up from molecules and nano-structures (“bottom-up”) versus the “top-down,” or miniaturization, approach. *Nano-* actually refers not so much to the size of the object as to the resolution at the molecular scale. At such small scales, about half of the atoms are in the surface layer, the surface energy dominates, and the surface layer can be considered a new material with properties different from those of bulk. The hierarchy of scales, both spatial and temporal, is represented in the following table:

	Scale			
	Quantum	Atom/nano	Mesoscopic	Macroscopic
Length (meters)	$10^{-11}$ – $10^{-8}$	$10^{-9}$ – $10^{-6}$	$10^{-6}$ – $10^{-3}$	$>10^{-3}$
Time (seconds)	$10^{-16}$ – $10^{-12}$	$10^{-13}$ – $10^{-10}$	$10^{-10}$ – $10^{-6}$	$>10^{-6}$

Classical surface and colloid chemistry generally treats systems experimentally in a statistical fashion, with phenomenological theories that are applicable only to building simplified microstructural models. In recent years scientists have learned not only to observe individual atoms or molecules but also to manipulate them with subangstrom precision. The characterization of surfaces and interfaces on nanoscopic and mesoscopic length scales is important both for a basic understanding of colloidal phenomena and for the creation and mastery of a multitude of industrial applications.



The self-organization or assembly of units at the nanoscale to form supramolecular ensembles on mesoscopic length scales comprises the range of colloidal systems. There is a need to understand the connection between structure and properties, the evolution and dynamics of these structures at the different levels—supramolecular, molecular, and submolecular—by “learning from below.”

When interaction and physical phenomena length scales become comparable to or larger than the size of the structure, as, for example, with polymer contour chain length, the system may exhibit unusual behavior and generate novel arrangements not accessible in bulk.

It is also at these levels (10–500 nm) that nature utilizes hierarchical assemblies in biology, and biological processes almost invariably take place at the nanoscale, across membranes and at interfaces. Biomolecular materials with unique properties may be developed by mimicking biological processes or modifying them. There is still much to discover about improving periodic arrays of biomolecules, biological templating, and how to exploit the differences between biological and nonbiological self-assembly.

The linkage of microscopic and macroscopic properties is not without challenges, both theoretical and experimental. Statistical mechanics and thermodynamics provide the connection between molecular properties and the behavior of macroscopic matter. Coupled with statistical mechanics, computer simulation of the structure, properties, and dynamics of mesoscale models is now feasible and can handle the increase in length and time scales.

Scanning probe techniques (SPM)—i.e., scanning tunneling microscopy (STM) and atomic force microscopy (AFM), as well as their variations—have the power to visualize nanoscale surface phenomena in three dimensions, manipulate and modify individual molecules, and measure such properties as adhesion, stiffness, and friction as well as magnetic and electric fields. The use of chemically modified tips extends the technique to include chemical imaging and measurement of specific molecular interactions. Improved optical methods complement probe images and are capable of imaging films a single molecule thick. Optical traps, laser tweezers, and “nano-pokers” have been developed to measure forces and manipulate single molecules. In addition, there is a vast range of experimental tools that cross different length and time scales and provide important information (x-ray, neutrons, surface plasmon resonance). Nevertheless, there is a further need for instrumentation of higher resolution, for example, in the decreased range of space and time encountered when exploring the dynamics and kinetics of surface films.

Chapter 1 is a view of the potential of surface forces apparatus (SFA) measurements of two-dimensional organized ensembles at solid–liquid interfaces. At this level, information is acquired that is not available at the scale of single molecules. Chapter 2 describes the measurement of surface interactions that occur between and within nanosized surface structures—interfacial forces responsible for adhesion, friction, and recognition.

In Chapter 3, Langmuir–Blodgett films of varying organizational complexity are discussed, as well as nanoparticles and fullerenes. Molecular dynamic simulation of monolayers and multilayers of surfactants is also reviewed. Chapter 4 presents those aspects of supramolecular layer assemblies related to the development of nanotechnological applications. Problems of preparing particle films with long-range two-dimensional and three-dimensional order by Langmuir–Blodgett and self-assembly techniques are dealt with in Chapter 5.

The next two chapters are concerned with wetting and capillarity. Wetting phenomena are still poorly understood; contact angles, for example, are simply an empirical parameter to quantify wettability. Chapter 6 reviews the use of scanning polarization force

microscopy (SPFM), a new application of AFM using electrostatic forces, to study the nanostructure of liquid films and droplets. The effect of solid nanometric deformation on the kinetics of wetting and dewetting and capillary flow in soft materials, such as some polymers and gels, is treated in Chapter 7.

Chapter 8 presents evidence on how the physical properties of colloidal crystals organized by self-assembly in two-dimensional and three-dimensional superlattices differ from those of the free nanoparticles in dispersion.

A biomolecular system of glycoproteins derived from bacterial cell envelopes that spontaneously aggregates to form crystalline arrays in the mesoscopic range is reviewed in Chapter 9. The structure and features of these S-layers that can be applied in biotechnology, membrane biomimetics, sensors, and vaccine development are discussed.

DNA is ideally suited as a structural material in supramolecular chemistry. It has sticky ends and simple rules of assembly, arbitrary sequences can be obtained, and there is a profusion of enzymes for modification. The molecule is stiff and stable and encodes information. Chapter 10 surveys its varied applications in nanobiotechnology. The emphasis of Chapter 11 is on DNA nanoensembles, condensed by polymer interactions and electrostatic forces for gene transfer. Chapter 12 focuses on proteins as building blocks for nanostructures.

The next two chapters concern nanostructured core particles. Chapter 13 provides examples of nano-fabrication of cored colloidal particles and hollow capsules. These systems and the synthetic methods used to prepare them are exceptionally adaptable for applications in physical and biological fields. Chapter 14, discusses reversed micelles from the theoretical viewpoint, as well as their use as nano-hosts for solvents and drugs and as carriers and reactors.

Chapter 15 gives an extensive and detailed review of theoretical and practical aspects of macromolecular transport in nanostructured media. Chapter 16 examines the change in transport properties of electrolytes confined in nanostructures, such as pores of membranes. The confinement effect is also analyzed by molecular dynamic simulation.

Nanolayers of clay interacting with polymers to form nanocomposites with improved material properties relative to the untreated polymer are discussed in Chapter 17.

*Morton Rosoff*

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# 1

## **Molecular Architectures at Solid-Liquid Interfaces Studied by Surface Forces Measurement**

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### **I. INTRODUCTION**

Molecular and surface interactions are ubiquitous in molecular science, including biology. Surface forces measurement and atomic force microscopy (AFM) have made it possible to directly measure, with high sensitivity, molecular and surface interactions in liquids as a function of the surface separation. Naturally, they have become powerful tools for studying the origins of forces (van der Waals, electrostatic, steric, etc.) operating between molecules and/or surfaces of interest [1–4]. They also offer a unique, novel surface characterization method that “monitors surface properties changing from the surface to the bulk (depth profiles)” and provides new insights into surface phenomena. This method is direct and simple. It is difficult to obtain a similar depth profile by other methods; x-ray and neutron scattering measurements can provide similar information but require extensive instrumentation and appropriate analytical models [4].

Molecular architectures are self-organized polymolecular systems where molecular interactions play important roles [5]. They exhibit specific and unique functions that could not be afforded by single molecules. Molecular architecture chemistry beyond molecules is not only gaining a central position in chemistry but becoming an important interdisciplinary field of science. Investigations of molecular architectures by surface forces measurement is important for the following reasons.

1. It is essential to elucidate intermolecular interactions involved in self-organization, whose significance is not limited to material science but extends to the ingenuity of biological systems [5].
2. The importance of surface characterization in molecular architecture chemistry and engineering is obvious. Solid surfaces are becoming essential building blocks for constructing molecular architectures, as demonstrated in self-assembled monolayer formation [6] and alternate layer-by-layer adsorption [7]. Surface-induced structuring of liquids is also well-known [8,9], which has implications for micro- and nano-technologies (i.e., liquid crystal displays and micromachines). The virtue of the force measurement has been demonstrated, for example, in our report on novel molecular architectures (alcohol clusters) at solid-liquid interfaces [10].
3. Two-dimensionally organized molecular architectures can be used to simplify the complexities of three-dimensional solutions and allow surface forces measurement. By

employing this approach, we can study complex systems such as polypeptides and polyelectrolytes in solutions. For example, it is possible to obtain essential information such as the length and the compressibility of these polymers in solutions by systematically varying their chemical structures and the solution conditions [11].

Earlier studies of surface forces measurement were concerned mainly with surface interactions determining the colloidal stability, including surfactant assemblies. It has been demonstrated, however, that a “force–distance” curve can provide much richer information on surface molecules; thus it should be utilized for studying a wider range of phenomena [12]. Practically, the preparation of well-defined surfaces, mostly modified by two-dimensional organized molecules, and the characterization of the surfaces by complementary techniques are keys to this approach. A similar concept is “force spectroscopy” [13], coined to address force as a new parameter for monitoring the properties of materials. A major interest in force spectroscopy is the single molecular measurement generally employing an atomic force microscope. This measurement treats relatively strong forces, such as adhesion, and discusses the binding of biotin-streptavidin [14] and complementary strands of DNA [15] as well as the unfolding and folding of proteins [16]. On the other hand, the forces measurement of two-dimensionally organized molecules has advantages complementary to those of single molecule force spectroscopy. It can monitor many molecules at the same time and thus is better suited for studying long-range weaker forces. The measurement should bear a close relevance to real systems that consist of many molecules, because interactions between multiple molecules and/or macroscopic surfaces in solvents may exhibit characteristics different from those between single molecules.

The aim of this review is to demonstrate the potential of surface forces measurement as a novel means for investigating surfaces and complex soft systems by describing our recent studies, which include cluster formation of alcohol, polyion adsorption, and polyelectrolyte brushes.

## II. SURFACE FORCES MEASUREMENT

Surface forces measurement directly determines interaction forces between two surfaces as a function of the surface separation ( $D$ ) using a simple spring balance. Instruments employed are a surface forces apparatus (SFA), developed by Israelachvili and Tabor [17], and a colloidal probe atomic force microscope introduced by Ducker et al. [18] (Fig. 1). The former utilizes crossed cylinder geometry, and the latter uses the sphere-plate geometry. For both geometries, the measured force ( $F$ ) normalized by the mean radius ( $R$ ) of cylinders or a sphere,  $F/R$ , is known to be proportional to the interaction energy,  $G_f$ , between flat plates (Derjaguin approximation),

$$\frac{F}{R} = 2\pi G_f \quad (1)$$

This enables us to quantitatively evaluate the measured forces, e.g., by comparing them with a theoretical model.

Sample surfaces are atomically smooth surfaces of cleaved mica sheets for SFA, and various colloidal spheres and plates for a colloidal probe AFM. These surfaces can be modified using various chemical modification techniques, such as Langmuir–Blodgett (LB) deposition [12,19] and silanization reactions [20,21]. For more detailed information, see the original papers and references texts.

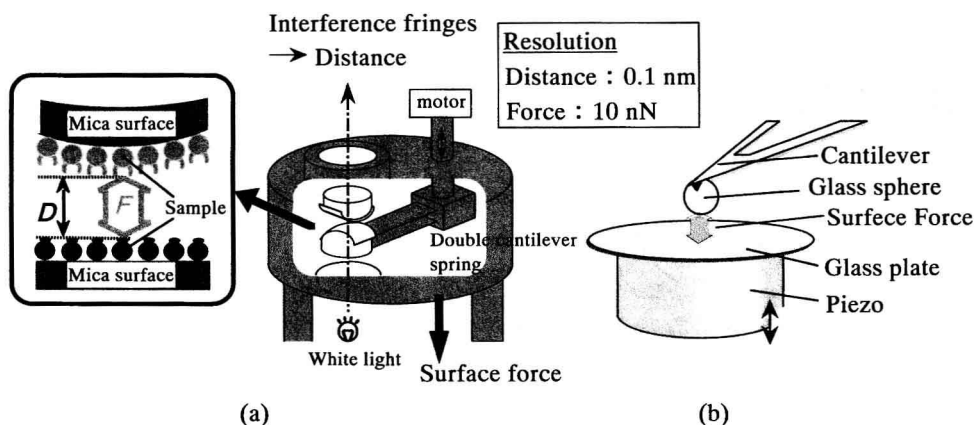


FIG. 1 Schematic drawings of (a) the surface forces apparatus and (b) the colloidal probe atomic force microscope.

### III. ALCOHOL CLUSTER FORMATION ON SILICA SURFACES IN CYCLOHEXANE

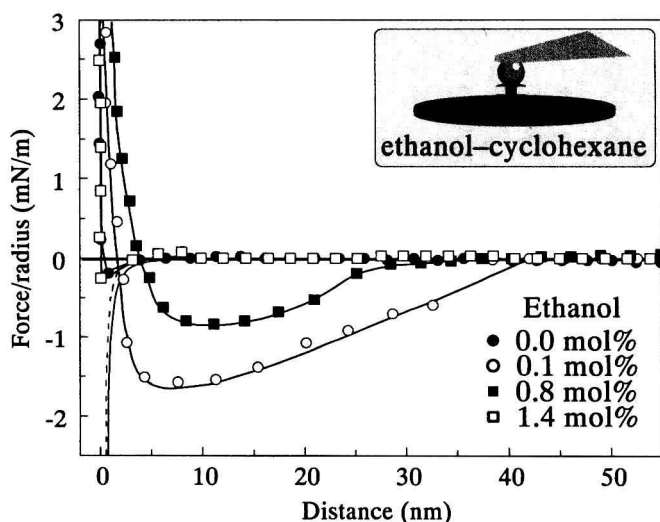
Surface forces measurement is a unique tool for surface characterization. It can directly monitor the distance ( $D$ ) dependence of surface properties, which is difficult to obtain by other techniques. One of the simplest examples is the case of the electric double-layer force. The repulsion observed between charged surfaces describes the counterion distribution in the vicinity of surfaces and is known as the electric double-layer force (repulsion). In a similar manner, we should be able to study various, more complex surface phenomena and obtain new insight into them. Indeed, based on observation by surface forces measurement and Fourier transform infrared (FTIR) spectroscopy, we have found the formation of a novel molecular architecture, an alcohol macrocluster, at the solid-liquid interface.

Adsorption phenomena from solutions onto solid surfaces have been one of the important subjects in colloid and surface chemistry. Sophisticated application of adsorption has been demonstrated recently in the formation of self-assembling monolayers and multilayers on various substrates [4,7]. However, only a limited number of researchers have been devoted to the study of adsorption in binary liquid systems. The adsorption isotherm and colloidal stability measurement have been the main tools for these studies. The molecular level of characterization is needed to elucidate the phenomenon. We have employed the combination of surface forces measurement and Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR) to study the preferential (selective) adsorption of alcohol (methanol, ethanol, and propanol) onto glass surfaces from their binary mixtures with cyclohexane. Our studies have demonstrated the cluster formation of alcohol adsorbed on the surfaces and the long-range attraction associated with such adsorption. We may call these clusters *macroclusters*, because the thickness of the adsorbed alcohol layer is about 15 nm, which is quite large compared to the size of the alcohol. The following describes the results for the ethanol-cyclohexane mixtures [10].

Typical forces profiles measured between glass surfaces in ethanol-cyclohexane mixtures are shown in Fig. 2. Colloidal probe atomic force microscopy has been employed. In pure cyclohexane, the observed force agrees well with the conventional van der Waals attraction calculated with the nonretarded Hamaker constant for glass/cyclohexane/glass,

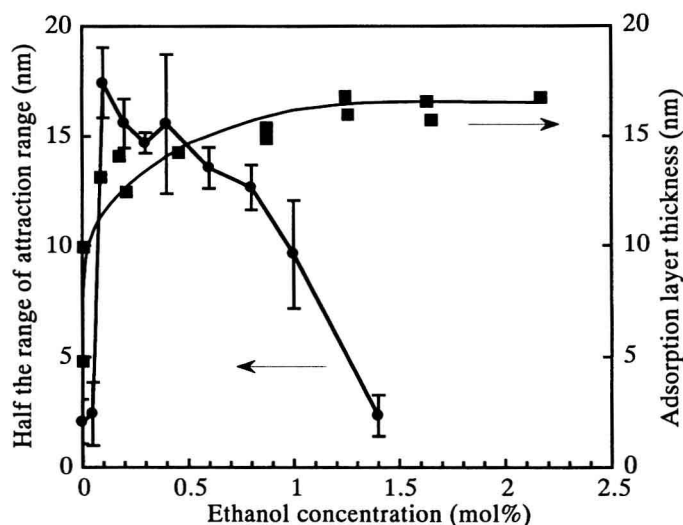
$3.1 \times 10^{-21}$  J. At an ethanol concentration of 0.1 mol%, the interaction changes remarkably: The long-range attraction appears at a distance of 35 nm, shows a maximum around 10 nm, and turns into repulsion at distances shorter than 5 nm. The pull-off force of the contacting surfaces is  $140 \pm 19$  mN/m, which is much higher than that in pure cyclohexane,  $10 \pm 7$  mN/m. Similar force profiles have been obtained on increasing the ethanol concentration to 0.4 mol%. A further increase in the concentration results in a decrease in the long-range attraction. At an ethanol concentration of 1.4 mol%, the interaction becomes identical to that in pure cyclohexane. When the ethanol concentration is increased, the range where the long-range attraction extends changes in parallel to the value of the pull-off force, indicating that both forces are associated with the identical phenomenon, most likely the adsorption of ethanol. Separation force profiles after the surfaces are in contact shows the presence of a concentrated ethanol layer near and on the surfaces (see Ref. 10a). The short-range repulsion is ascribable to steric force due to structure formation of ethanol molecules adjacent to the glass surfaces.

In order to understand the conditions better, we determined the adsorption isotherm by measuring the concentration changes in the alcohol upon adsorption onto glass particles using a differential refractometer. Figure 3 plots the range of the attraction vs. the ethanol concentration, together with the apparent adsorption layer thickness estimated from the adsorption isotherm, assuming that only ethanol is present in the adsorption layer [22]. For 0.1 mol% ethanol, half the distance where the long-range attraction appears,  $18 \pm 2$  nm, is close to the apparent layer thickness of the adsorbed ethanol,  $13 \pm 1$  nm. This supports our interpretation that the attraction is caused by contact of opposed ethanol adsorption layers. Half the attraction range is constant up to  $\sim 0.4$  mol% ethanol and decreases with increasing ethanol concentration, while the apparent adsorption layer thickness remains constant at all concentration ranges studied. The discrepancy between the two quantities indicates a change in the structure of the ethanol adsorption layer at concentrations higher than  $\sim 0.4$



**FIG. 2** Interaction forces between glass surfaces upon compression in ethanol-cyclohexane mixtures. The dashed and solid lines represent the van der Waals force calculated using the nonretarded Hamaker constants of  $3 \times 10^{-21}$  J for glass/cyclohexane/glass and  $6 \times 10^{-21}$  J for glass/ethanol glass, respectively.





**FIG. 3** Plots of half the range of attraction (see Fig. 2) and the apparent thickness of the ethanol adsorption layer vs. the ethanol concentration.

mol%. The structures of the adsorbed ethanol turned out to be hydrogen-bonded clusters, via the study employing FTIR-ATR spectroscopy.

FTIR-ATR spectra were recorded on a Perkin Elmer FTIR system 2000 using a TGS detector and the ATR attachment from Grasby Specac. The ATR prism made of an oxidized silicon crystal was used as a solid adsorbent surface because of its similarity to glass surfaces. Immediately prior to each experiment, the silicon crystal was treated with water vapor plasma in order to ensure the formation of silanol groups on the surfaces. Obtained spectra have been examined by referring to well-established, general spectral characteristics of hydrogen-bonded alcohols in the fundamental OH stretching region, because ethanol is known to form hydrogen-bonded dimers and polymers (clusters) in nonpolar liquids [23]. We have also experimentally examined hydrogen-bonded ethanol cluster formation in bulk cyclohexane-ethanol mixtures using transmission infrared spectroscopy.

FTIR-ATR spectra of ethanol in cyclohexane at various ethanol concentrations (0.0–3.0 mol%) are presented in Figure 4. At 0.1 mol% ethanol, a narrow negative band at  $3680\text{ cm}^{-1}$ , a weak absorption at  $3640\text{ cm}^{-1}$  (free OH), and a broad strong absorption ( $3600\text{--}3000\text{ cm}^{-1}$ ) with shoulders at  $3530\text{ cm}^{-1}$  (cyclic dimer or donor end OH),  $3450$ , and  $3180\text{ cm}^{-1}$  are observed. It is known that the isolated silanol group exhibits an absorption band at  $3675\text{--}3690\text{ cm}^{-1}$  in a nonpolar liquid, e.g.,  $\text{CCl}_4$  and when the silanol groups hydrogen bond with esters, the absorption band shifts to a lower wavenumber ( $3425\text{--}3440\text{ cm}^{-1}$ ) [24]. Thus, the negative absorption at  $3680\text{ cm}^{-1}$  and the positive shoulder at  $3450\text{ cm}^{-1}$  should correspond to the decrease in the isolated silanol groups and the appearance of the silanol groups hydrogen bonded with the adsorbed ethanol, respectively. The strong broad band ascribed to the polymer OH appeared at  $3600\text{--}3000\text{ cm}^{-1}$  together with the relatively weak monomer OH band at  $3640\text{ cm}^{-1}$ . This demonstrated the cluster formation of ethanol adsorbed on the silicon oxide surface even at 0.1 mol% ethanol, where no polymer peak appeared in the spectrum of the bulk solution at 0.1 mol% ethanol. With increasing ethanol concentration, the free monomer OH ( $3640\text{ cm}^{-1}$ ) and the polymer OH peak ( $3330\text{ cm}^{-1}$ ) increased, while the peaks at  $3530$ ,  $3450$ , and  $3180\text{ cm}^{-1}$  remained the same.