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A perspective on surfaces and interfaces

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The importance of surfaces and interfaces cannot be overstated, with their reach extending from the hardware of the digital age to the processes of life. The past half-century has seen the development of a full and varied toolkit for characterizing them. This toolkit is now serving a growing interdisciplinary community and is providing a powerful platform for scientific research and manufacturing technology.

Surfaces and interfaces are ubiquitous. They are found in systems as simple as a piece of metal in a vacuum, and as complex as biological cells and living organisms. They define a boundary with the surrounding environment and influence interactions with that environment, and so it is no surprise that interfaces have been appreciated historically — just think of how corrosion, tarnishing and friction have plagued the hardware of civilization. But a cursory scan of the scientific and technological literature shows that the direct study of real surfaces is a fairly recent phenomenon. It is only over the past decade or so that the subject of interfaces has moved to the forefront of an increasing number of fascinating fundamental scientific enquiries. The ability to precisely engineer interfaces is playing an increasingly dominant part in the development of new technologies relevant to all aspects of our lives, from energy production to biomedical implants.

I think it is useful to look back and consider how we arrived at this point, not least because it serves as an interesting example of how science often evolves slowly during years of patient study, followed by a sudden explosion in the number of new insights and new applications. In the case of interface science, it is not that many years ago when there still were no tools available to us for directly interrogating the tiny amounts of matter present in surfaces and interfaces. The mass balance, which had been such a powerful instrument for early chemists, was incapable of measuring the mass of a surface layer. But today, it is almost taken for granted that we can directly image and even control single atoms and molecules on a surface and create useful new structures. These endeavours are supported by continuously evolving theories, which are in turn bolstered by the dizzying increase in the power of computers so that simulations now routinely help unravel the details of interface phenomena, such as the behaviour of fluids in confined spaces while flowing across chemically structured surfaces. When I consider these achievements and my journey with a large number of colleagues down the path of surface and interface research over the past four decades, I am truly struck by the confluence of what at one time were considered wholly different streams of science. The articles that follow in this issue give an excellent demonstration of how the merging of different scientific streams has given us a commanding toolbox, which makes it possible to advances the frontiers of interface science and technology in fields as diverse as electronics, cell biology and sensor development.

In my mind, the need to understand in detail surfaces and interfaces and to control them really heightened in the first half of the past century. At that time, machinery — particularly automobiles — became an increasingly important factor in our economy so that developing methods for controlling phenomena such as friction, lubrication, adhesion, wetting, corrosion and surface oxidation provided opportunities for enormous economic gains. Although incisive experimental tools for probing surfaces were developed only later, scientists and engineers nevertheless had useful chemical and physical concepts on hand to guide their thinking. In fact, a number of important surface and interface-related phenomena were uncovered during this period, including the mechanism of the photo-electric effect and the invention of the transistor. Reasonably accurate concepts were also developed for interfacial phenomena involving soft matter, such as the self-organization of a monolayer of amphiphilic (surfactant) molecules at metal surfaces as relates to lubrication, wetting and adhesion[1,2].

New developments

But the true birth of surface and interface science, where molecular and atomic details of a surface are imaged and manipulated directly, occurred only in the second half of the past century. As has been nicely outlined in a historical perspective by Duke[3], the birth and subsequent evolution of surface science were driven by technological innovations. Only when ultra-high vacuum systems became available in the 1960s was it possible to create and maintain well-defined surfaces. Still, the direct and quantitative determination of the atomic composition and structure of clean metal surfaces under vacuum conditions had to await the development of electron and ion spectroscopies, which occurred in electrical engineering and physics labs during the 1960s to 1980s. These efforts to uncover the atomic details of surfaces coincided with investigations of molecular self-assembly at surfaces, which started in the early 1980s and was enabled in good part by the emergence of photon-based surface characterization tools, such as monolayer sensitive infrared, optical and photoelectron spectroscopies.

During this time, I was working on surface molecular assembly at Bell Laboratories, surrounded by many of the vacuum-surface science pioneers of the time. But our direct interaction was really surprisingly small, with the experimental hardware and concepts needed to drive the vacuum side of surface science firmly rooted in physics and the molecular side in chemistry[4]. What overlap there was proved, of course, to be extremely stimulating. Overall, however, vacuum-surface science — or 'hard' surface science because of its focus on bare single crystals of metal — was evolving along its own course, while molecular surface assembly headed off in another direction to become the 'soft' surface science concerned with the behaviour of molecules such as surfactants and even polymers at interfaces[5].

Developments in the hard surface science have given us ever faster computers and communication technologies. Evolution of the soft interface science has opened avenues for studying biological interfaces and, in the late 1980s, kick-started 'soft lithography' as a simple and versatile lab-bench method for chemical patterning of surfaces down to submicrometre dimensions. Intriguingly, processing capabilities of hard surface science have been combined with soft lithography to con-

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trol the wetting behaviour of fluids under confinement and on chemically patterned surfaces. These so-called microfluidic systems, which first emerged in the early 1990s, are now mainly created by simple soft lithography methods and have been applied to a wide range of analytical and sensing systems. Yet another stream of scientific development appeared in the mid to later 1980s, when chemists began to learn to control the precipitation of simple inorganic compounds from solution to create uniform, nanometre-sized crystallites. Such crystallites or colloidal particles with nanometre-scale dimensions have been produced and used throughout history. For example, gold colloids were used for decorating pottery or staining glass, and silver colloids formed the basis of photographic film. But transforming the production of particles from a highly empirical art to a rational, adjustable method was only possible when the principles developed to explain wetting and surface molecular assembly were used to explore the factors that control the sizes, shapes and properties of colloidal nanoparticles. This has made it possible to achieve impressive control over nanoparticle formation, to the extent that we can now produce nanoparticles with narrow size distributions, alter the shape of particles by selective growth of appropriate crystal faces and tune particle properties such as their optical response.

The contemporary toolkit

While each of these several fields was evolving separately, the ability to routinely observe and even manipulate individual objects at the nanometre scale remained tantalizingly out of reach. Although electron microscopy had been around for decades, it could not be used for many samples and problems. The advent of scanning probe microscopies (SPM) filled this gap and has over the course of the 1990s and into the present, revolutionized surface and interface science (and, incidentally, seems to have prompted the arrival of 'nanotechnology' as the label of choice for every study looking at something 'small'). The first SPM studies looked at 'hard' surfaces that are of interest for microelectronics and heterogeneous catalysis, revealing the atomic structure of single crystals held in vacuum. Studies then also shifted to 'soft' systems to explore self-assembled molecules at surfaces. Nowadays, even surfaces immersed in liquid can be imaged using SPM. This capability, along with the emergence of non-linear laser spectroscopies that are sensitive to wet interfaces, has started to provide incisive access to biological interface problems.

Another crucial aspect of the development of surface and interface science is the emergence of computational tools that make it possible to use evolving theory, ranging from quantum to statistical mechanics, to tackle simulations and analyses of enormously complex interfacial behaviour. In a field that has mainly emerged from empirical observations and experiment, it is now not unusual to see that well-executed theory and simulation can be accepted as more useful than experiment (which is often prohibitively costly and difficult for complex systems and phenomena).

What seems amazing to me is that hard and soft surface and interface science have delivered a powerful range of common experimental and theoretical tools that are proving useful in areas as diverse as microelectronics and biocompatibility. Groups of scientists from diverse backgrounds have access to these tools for very different investigations and can think in a common way about diverse surface and interface phenomena and applications. The following articles illustrate some of the tools, concepts and knowledge that are now readily available to those who study interfaces and engineer interfacial phenomena and structures for practical applications.

Chandler (p. 640) gives an example of how well-constructed theory can help to identify the basic structural and energetic factors that control the behaviour of water at hydrophobic surfaces and thereby develop a powerful yet simple understanding of an often complex phenomenon that affects a wide range of systems and processes. This approach to understanding the interfacial behaviour of liquids will accelerate progress in developing applications for microfluidics and bio-membranes, and bring the understanding of fundamental phenomena such as wetting to new levels. Considering engineered device structures, Atencia and Beebe (p. 648) show that the ability to build micrometre-to-nanometre-scale channel structures provides a means to exploit the fundamental principles of fluid behaviour in confined geometries. The result is a wide range of useful microfluidic devices that harness interface effects. Moving towards softer, biologically relevant structures, Tanaka and Sackmann (p. 656) detail strategies for constructing and using improved model cell membranes. These essentially self-organized molecular layers, tethered to surfaces, are coupled with analytical probes to study fundamental processes occurring in or on biological membranes and developed for sensor applications. These last two papers point to a distinct change in the ability to use fundamental knowledge for bioengineering. Yin and Alivisatos (p. 664) review the rapid progress that has been made in forming nanometre-sized crystallites of inorganic materials with excellent control over their sizes and shapes. They show that fundamental kinetic and thermodynamic principles, along with judicious use of molecular adsorption at the crystallite surface, allow us to select growth pathways to achieve the controlled formation of unprecedently complex inorganic nanostructures. Finally, Barth, Costantini and Kern (p. 671) give us a look at how the traditional area of vacuum-surface science with single crystal surfaces has evolved into a highly sophisticated art. Again, kinetic and thermodynamic principles are used to precisely control the formation of complex ordered surface structures that might find use in the information industry. Overall these articles underscore the importance of the confluence of surface and interface research in recent years and point the way to future developments and applications. ■

1. Bowden, F. P. & Tabor, D. in *The Friction and Lubrication of Solids* (Oxford Univ., Oxford, 2001).
2. Baier, R. E., Shafrin, E. G. & Zisman, W. A. Adhesion, mechanisms that assist or impede it. *Science* **162,** 1360–1368 (1968).
3. Duke, C. B. The birth and evolution of surface science: Child of the union of science and technology. *Proc.Natl Acad. Sci. USA* **100,** 3858–3864 (2003).
4. Ulman, A. Formation and structure of self-assembled monolayers. *Chem. Rev.* **96,** 1533–1554 (1996).
5. Love, J. C., Estroff, L. A., Kriebel, J. K., Nuzzo, R. G. & Whitesides, G. M. *Chem. Rev.* **105,** 1103–1169 (2005).

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