MOLECULAR FORCES AND SELF ASSEMBLY

Challenging the cherished notions of colloidal theory, Barry Ninham and Pierandrea Lo Nostro confront the scientific lore of molecular forces and colloidal science in an incisive and thought-provoking manner. The authors explain the development of these classical theories, discussing, amongst other topics, electrostatic forces in electrolytes, specific ion effects and hydrophobic interactions. Throughout the book, they question assumptions, unearth flaws and present new results and ideas. From such analysis, a qualitative and predictive framework for the field emerges; the impact of this is discussed in the latter half of the book, through force behaviour in self assembly. Here, numerous diverse phenomena are explained, from surfactants to biological applications, all richly illustrated with pertinent, intellectually stimulating examples. With mathematics kept to a minimum, historical facts and anecdotes woven through the text, this is a highly engaging and readable treatment for students and researchers in science and engineering.

Barry W. Ninham, a pioneer of modern theory describing molecular forces, interactions and self assembly, is currently Professor Emeritus of the Department of Applied Mathematics at the Australian National University (ANU). He has been an active researcher for over 40 years, over which time he has authored or co-authored seven books and more than 400 technical papers. He has received numerous awards, including the Ostwald Award of the German Chemical Society (2005), the Swedish Erlander National Chair of Chemistry (1998), and, in 2008, ANU created the Barry Ninham Chair of Natural Sciences Award to recognize his contributions.

Pierandrea Lo Nostro is a Research Fellow and Teacher in the Department of Chemistry at the University of Florence, from where he received his Ph.D. in Chemical Sciences in 1992. His current research interests include macromolecular self assembly, self assembly of biocompatible surfactants specific ion effects (Hofmeister series) and nanomaterials.

Cambridge Molecular Science

As we move further into the twenty-first century, chemistry is positioning itself as the central science. Its subject matter, atoms and the bonds between them, is now central to so many of the life sciences on the one hand, as biological chemistry brings the subject to the atomic level, and to condensed matter and molecular physics on the other. Developments in quantum chemistry and in statistical mechanics have also created a fruitful overlap with mathematics and theoretical physics. Consequently, boundaries between chemistry and other traditional sciences are fading and the term *Molecular Science* now describes this vibrant area of research.

Molecular science has made giant strides in recent years. Bolstered by both instrumental and theoretical developments, it covers the temporal scale down to femtoseconds, a time scale sufficient to define atomic dynamics with precision, and the spatial scale down to a small fraction of an Angstrom. This has led to a very sophisticated level of understanding of the properties of small molecule systems, but there has also been a remarkable series of developments in more complex systems. These include: protein engineering; surfaces and interfaces; polymers; colloids; and biophysical chemistry. This series provides a vehicle for the publication of advanced textbooks and monographs introducing and reviewing these exciting developments.

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In Colloid, Nano Sciences and Biology

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and

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Preface

This book outlines developments in physical and colloid chemistry over the last decade or two that have changed our understanding of molecular forces and the self assembly of amphiphilic molecules. Within the sciences, a subject or discipline is defined by a freemasonry, the members of which are united by a common lore. The received beliefs of adepts are reaffirmed by recitation and repetition of the lore, and reinforced by the weight of authority embodied in the literature of the discipline. The more venerable the literature, the more conservative is the freemasonry. Challengers to the canon are at first dismissed as heretics or apostates, but if, later, their claims are conceded to have validity, they and their theories are eventually accepted into the fold. The discipline moves on. So, the advocates of a once revolutionary Darwinism, wrongly defined by others by the trite aphorism 'survival of the fittest', retreated into convoluted defences of the dogma, represented by the elegant writings of Stephen J. Gould. Two decades ago the notion that environmental influences such as temperature could affect gene expression invited the ridicule attending to an earlier Lamarkism. Similarly for any questioning of the dogma of the Weissman barrier in immunology. Not any more.

The origins of the discipline of modern physical chemistry can probably be dated most conveniently to Napoleon's scientific expedition to Egypt 200 years ago. Berthelot, one of the expedition's scientists, observed on the receding flood plain of the Nile rocks that were covered with soda lime, sodium carbonate. This was a mystery. Sodium chloride in the Nile waters ought to have stayed in solution and it was calcium carbonate that should have precipitated out. But at the high temperatures of the Egyptian summer to which the rocks were exposed and with desiccation the reaction is reversed (with catastrophic consequences to the Sphinx). So began the notion of temperature (and 'water structure') as controlling variables. Physical and colloid and surface chemistry evolved over the intervening 200 years into a central, enabling discipline of modern science and engineering. Its theories provide an intuition, and its experimental techniques underlie and provide unquestioned support for the work of many other disciplines, from biological to chemical engineering, agricultural and earth sciences.

The interpretation of a measurement depends on a theory. But if the theory is flawed or wrong, so also is the meaning of the measurement. The deficiencies propagate. For a long time adepts of physical chemistry held to a world view that became rigid, dated and lacked predictability. The realization that our theories and intuition were seriously flawed and often misleading occurred gradually over the last 40 years, but the deficiencies became increasingly obvious over the last decade. In that decade a flurry of activity has uncovered defects in the foundations. We have gone some way towards remedying them. A new intuition has been built and is evolving further. From a practical viewpoint, how to exploit this new intuition and put forces to work, the ramifications are large. To say that the developments described in this book are radical is to put the matter too mildly. The background is described in Chapter 1.

We have avoided mathematics as far as possible: on the grounds that those who do not speak the language of mathematics and physics would be none the wiser for its inclusion. For readers who do speak that language it would be superfluous, as the technicalities can easily be tracked down via the literature cited.

There are many good books available that give accounts of overlapping areas in what we might now be entitled to call the 'old' theories of physical chemistry and colloid science. Of the more recent books, those of J. N. Israelachvili [1], D. F. Evans and H. Wennerström [2], V. A. Parsegian [3], R. J. Hunter (*Introduction to Modern Colloid Science*) [4] and O. G. Mouritssen (*Life – As a Matter of Fat*) [5] on lipids are just a few. Some old books, such as Robinson and Stokes [6], Harned and Owen [7] and Friberg et al. [8], still stand. A book by one of us with J. Mahanty [9] developed all the necessary formalism to extend Lifshitz theory and its applications in 1976. Another, by S. T. Hyde et al. [10], is vast in scope and reasonably up to date, on self assembly.

A difficulty is that most of the content of such very good books that inform the discipline give accounts of our knowledge of molecular forces and self assembly that were unquestioned up to 10 years ago. But those theories are now out of date and can be quite misleading. The idea that venerable fundamentals such as pH, pK_as, buffers, ion binding, membrane potentials, ion transport and the classical DLVO theory of colloid stability might have to be revisited, or even scrapped, would have seemed absurd then. Events have moved fast and the long-standing picture of the adepts that included ourselves is certainly no longer valid.

We acknowledge Drew F. Parsons (Australian National University, Canberra) for his invaluable contribution to Chapter 7, where the effects due to dispersion forces are discussed in detail and quantified.

Acknowledgements (B. W. N.)

I owe a debt to R. B. Dingle, who pioneered modern asymptotics, taught me physics and analysis and sent me from the other side of the world from Western Australia to America 50 years ago to study for a PhD in statistical mechanics with Elliott W. Montroll. The scientific world then was a smaller place. Everyone knew everyone, and they knew the genealogy and the history of ideas. It was Elliott who encouraged me to develop this field. Ten years on my friend George H. Weiss allowed me the opportunity of a long sabbatical leave at the National Institutes of Health in Washington. V. Adrian Parsegian and I began there a seminal, tremendously exciting and lasting collaboration on molecular forces in colloid science and biology.

A result of that work was an invitation from my subsequent boss, Sir Ernest Titterton, who pressed the button on the first nuclear bomb explosion, to set up a new Department of ‘Applied Mathematics’ in the Institute of Advanced Studies at the Australian National University in Canberra. His own mentor, Sir Mark Oliphant, had worked with Rutherford, discovered tritium, was intimately involved with the bomb which he later bitterly regretted and with radar; and was involved in founding the Pugwash conferences. Mark was a founding father of the ANU. When he was compulsorily retired at the grand old age of 65, I gave him haven in the new Department. In return he sometimes gave me advice.

We were not allowed to teach undergraduates or to apply for research grants. ‘Applied Mathematics’ was defined by me to mean colloid and surface chemistry, and optical sciences. My responsibilities were to do exactly what I pleased. Colloid science was then a poor cousin of physical chemistry; now it struts the stage under a new name, nanotechnology. (Its attractiveness to ANU was in part because of the in-house invention of Synroc for nuclear waste disposal. Success depends on compaction from solution of the colloidal nuclear waste ceramic, a matter of specific ion effects that figure largely in this book.)

From its foundation in 1969, the Department grew and grew. I do not know how because we had no money, but somehow we acquired enough. Oliphant said it was better that way and he was right. The Department became an eclectic international interdisciplinary centre of experimentalists and theoreticians, pure and applied researchers, physicists, chemists, mathematicians, biologists and chemical engineers that still continues after 40 years as successfully as ever. It was a different world and I owe more than I can say to ANU.

Over a period of 30 years or so I was privileged to recruit, to supervise, to mentor, to direct and work with successive waves of astonishingly talented PhD students and young scientists from Australia and many other countries. They came because we had time to think and do science unencumbered. At least 60 of them became senior professors in various countries and disciplines.

I want to express my thanks for seminal interactions with those who introduced me to new fields and taught me things I did not know, especially Stephen Hyde, Kåre Larsson and Sten Andersson, D. John Mitchell and Jacob Israelachvili. I am indebted to them all, as I am to several hundred PhD students, research colleagues and visitors. I hope they will forgive me if I do not list them all.

Besides the ANU, and the NIH, various universities and research institutes gave me respite to work for long periods as a visiting professor without administration and surrounded by students.

In the USA: U. Minnesota; in France: CEA Saclay, the College de France; U. Paris V1; in Sweden: U. Lund, YKI, KTH, Chalmers, and Malmo; in Italy: U. Florence and Cagliari; in Germany: U. Regensberg. My hosts and collaborators who made that luxury possible were: D. Fennell Evans; Tom Zemb and Marie- Paule Pileni; Sten Andersson, Bjorn Lindman, Kåre Larsson and Hakan Wennerstrom, Krister Holmberg and Per Cleasson, Roland Kjellander, Bengt Nordén and Zoltan Blum; Werner Kunz and Maura Monduzzi.

Most importantly Piero Baglioni at the University of Florence gave the two of us the opportunity to work together over the last five years in Florence and we are in his debt.

This book owes much to two earlier books [9,10].

The first contains theory that we shall use, and is mathematically abstruse. Some important parts of it that are relevant are unavailable elsewhere. Unfortunately the book is long out of print and mathematically difficult, so that work still valid 30 years ago is rediscovered in every decade.

The second book sweeps over enormous territory, but the price is out of reach to all but the richest libraries.

Work on complex self assembly and structure in biology and materials sciences and its systemization is moving fast, and we refer the reader to the websites of Sten Andersson and of Stephen T. Hyde to obtain a glimpse of astonishing new worlds of science.

Acknowledgements (P. L. N.)

It is fascinating, during a long walk up in the mountains, to stop, turn back and contemplate not only the scenario in front, but also the narrow and sometimes difficult footpath that we have covered. This book offers me now this opportunity.

Unquestionably my professional experience has the imprint of Enzo Ferroni, my true master at the University of Florence, and the first pioneer in Italy in colloid and interface science. He did not simply contaminate me with his curiosity and passion for physical chemistry, to me the most complete, embracing and appealing discipline among the chemical sciences. His words, proximity and example were

the seeds that found a fertile humus in my mind. Briefly, he introduced me to what Maxwell named as 'crossed fertilization' between different aspects (disciplines) of the real world. This attitude has become for me a sort of polar star. And this is why I accepted the challenge to write this book with Barry W. Ninham.

During my PhD I got the chance to work with Sow-Hsin Chen and others at MIT, where my studies on lecithins and fluorinated alkanes began. And since that time I have been focusing my interests on the role of the solvent in self assemblies.

Then the American experience continued at the University of South Florida, where Jack E. Fernandez introduced me to vitamin C amphiphilic derivatives and to their properties.

After my return to Florence, I continued working at the Department of Chemistry with my friend Piero Baglioni. In the following years our group has been growing with excellent younger researchers. Their scientific skills and close friendship support and stimulate my current activity.

My friendship and collaboration with Barry W. Ninham started in 1997. Again, his vibrant passion for unsolved or formerly-solved-but-not-really-so-now issues prompted me to approach the mysterious Hofmeister phenomena. This almost unknown topic – although clearly ubiquitous – goes straight to the core of chemistry, as it reflects the fact that matter is not simply made up of differently coloured ping-pong balls and springs, but behaves in 'specific' ways that can now be understood – at least partially – in terms of intermolecular forces. And that water is not simply a homogeneous and molecularly smooth environment where soluble entities diffuse, but it directly participates at the molecular level in physicochemical phenomena. I learnt from Barry W. Ninham an honest and youthful energy in trying to understand without accepting apparently consolidated, ready-to-use (*ipse dixit*) recipes, not even when they are named after eminent scientists. Any theory is a partial look at a small piece of the world, waiting to be corrected, expanded and fully understood. After all, real science is a well-equipped gym of humility. I recognize that this oxymoron – i.e. accepting, checking and sometimes rejecting the conceptual milestones that our forerunners bequeathed us – is vital to scientists, and opens wide the gate of experimental sciences to the young researchers, giving a glimpse of a much larger horizon.

In the end, this was our wish and we hope that our task will promote debate and curiosity in others.

Front cover illustration

Fresco by Fra' Beato Angelico, fifteenth century, Museum of San Marco, Firenze. The two images on the front cover (courtesy of Piero Baglioni) show the original, damaged by the Arno River floods of 4 November 1966, and the restoration by

Dino Dini. The non-invasive techniques of restoration developed by Professor Enzo Ferroni, at the University of Florence, are a classic exemplar of nanotechnology in action. They have been developed further for preservation of ancient manuscripts. Similar techniques were used by the Mayan civilization. The methods use molecular forces, self-assembled microemulsions, nanoparticle synthesis, water structure and specific ion effects. See P. Baglioni and co-workers, Ref. 11.

31 March 2009, Firenze and Canberra.

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