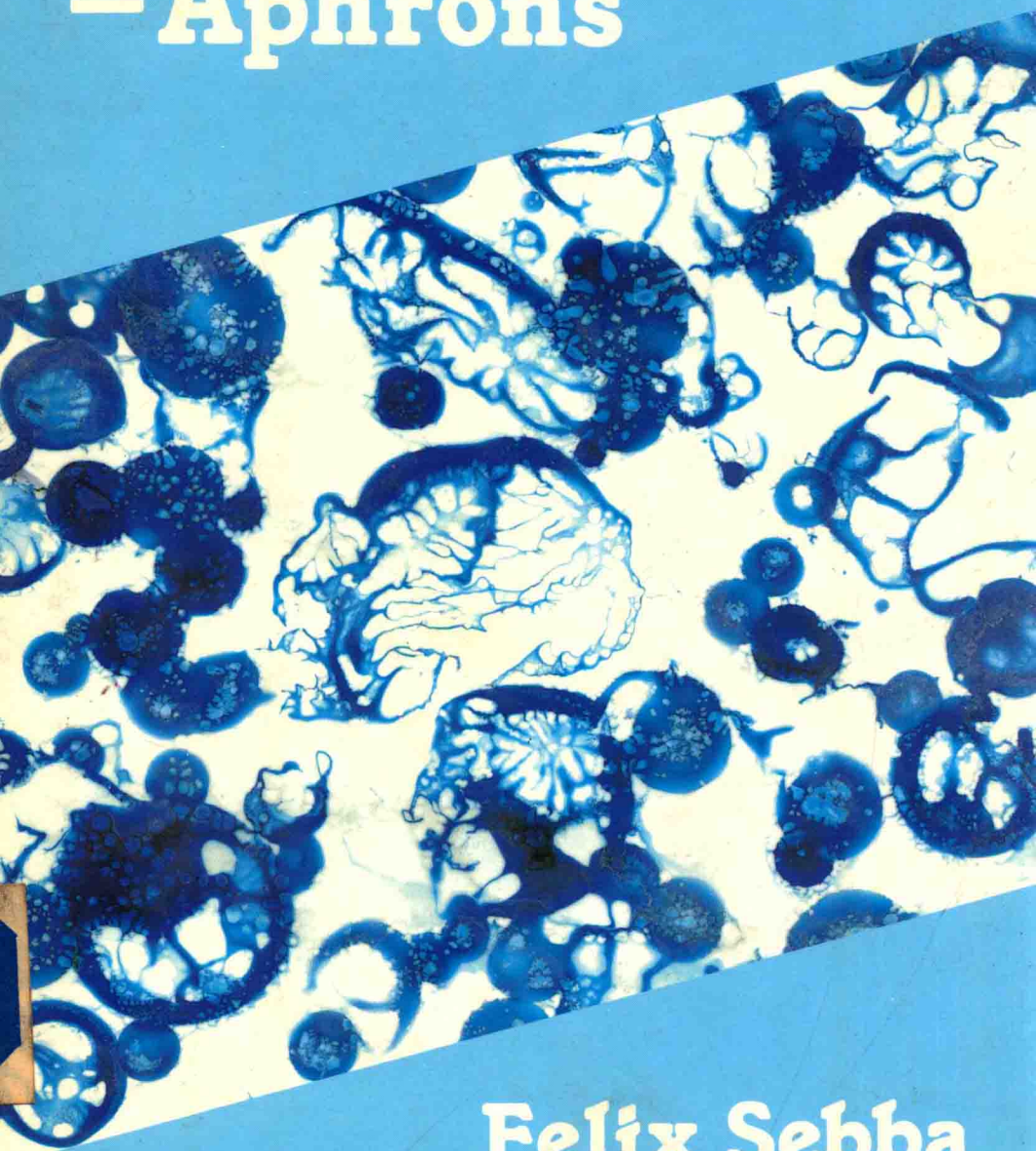


Foams and Biliquid Foams — Aphrons



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CHAPTER 1

Introduction

For a scientist, whose personal satisfaction is derived from experiments in his laboratory, there must be a powerful motivation for him to tear himself away from his laboratory in order to write a book. In this case the motivation was the realization that there was an important gap in the literature on surface chemistry which needed filling. This was the absence of any book on the fluid-fluid interface at a level sufficient for a novice in the field to acquire enough of the fundamentals of the subject to be able to understand the important phenomena which occur at the liquid-gas and liquid-liquid interfaces. Because of the importance of solid interfaces in catalysis and solid-state devices, this area has a voluminous literature, but fluid interfaces have been sadly neglected even though these interfaces play an important role in many engineering phenomena and particularly in biological phenomena. Therefore, it is necessary to have an introduction to the fundamental physics and chemistry which occur at such interfaces at a level suitable for the non-specialist in the field. This book is an attempt to fill that gap, but it goes even further in that it reports some interesting advances in the area, some of which have not yet been reported in the general literature.

Since the time of Dalton, the growth of chemical sciences and those dependent upon them has been based upon an atomic and, subsequently, a molecular view of matter, and there can be no gain-saying how successful this has been. We live in a world which has been shaped, whether for good or evil, by the advances made in chemistry and the momentum created by these shows no sign of diminishing. Because of this success, it has become almost axiomatic that, in order to understand matter in all its forms, all we need to

know is the molecular structure and the forces operative between molecules. However, there are still many mysteries which elude explanation and of these the most challenging is 'What are the forces responsible for life?' Stimulated by the growth of chemical knowledge and the availability of remarkably sensitive instruments developed by physicists, the advances in biology, particularly in this century, have been momentous. Nevertheless, attempts to explain living behaviour in terms of the simple forces which operate for inanimate matter have been singularly unsuccessful. The time is now opportune for us to ask ourselves whether we have been missing something important, the understanding of which would enable us to understand life better. It will be one of the objectives of this book to draw attention to one factor which has been neglected and which might play an important part in helping us to understand what activates living matter: the role of surface forces and surface-active molecules.

Advances in biology have been built upon the concept of the cell as the unit of living matter, and then, when the complexity of the cell was better appreciated, upon smaller units, the organelles. It has always been felt that the properties of organelles could be fully explained when the composition and behaviour of the component molecules were completely understood. However, although the biochemists have made fantastic strides in understanding the conversion of one biomolecule into another, and the biophysicists and molecular biologists have made great advances in explaining how genetic information is transferred from a cell to its progeny, the problem still remains of how the biomolecules change from inanimate structures to the dynamic arrangements which show the properties associated with life. While it is partly understood how genetic information can be translated into specific molecules, it is not understood how the shapes of these molecules are related to their functions, or how movement within or between cells comes about.

However, this book is not a treatise on biology. The biological implications simply emerge as part of a larger enquiry into the properties associated with particles of a size said, very imprecisely, to be of colloidal dimensions. This is the range of size at which surface forces begin to become more important than other forces such as gravity. Particles of such size play an important part in inanimate systems, many of which are just as poorly understood as are biological systems. Some of these are of industrial importance, to mention only emulsions, slurries, pastes, and sludges. These all have two factors

in common. In the first place they are multi-phase systems of which one phase is water. This means that they have interfaces between the phases. As a consequence surface forces play an important role in determining how they will behave. In addition, as they are usually concentrated systems, the regions between the phases are often very thin, and thin aqueous films have some unexpected properties.

In recent years there has been a renewed interest in surfaces and surface forces, but these have tended to focus attention on solid surfaces, partly because instruments are available which facilitate their study, and also because of the importance of solid-state electronic devices. Another area involving the solid-fluid interface is that of heterogeneous catalysis and scientific advances in that field are steadily progressing. The neglected areas are those of the liquid-liquid and liquid-gas interfaces, and yet it is here that understanding is required if some of the problems mentioned above are to be resolved.

This book is not intended to be a treatise on these interfaces, although it will deal with some aspects of them. It is an introduction to, and discussion of, a novel arrangement of multiple-phase systems, which it is believed may be quite widespread in its occurrence but has not hitherto been accurately defined. This arrangement combines the surface forces operative in colloid systems with the properties of thin aqueous films. This produces a system of extraordinary vitality which is already showing considerable potential for chemical operations. Perhaps of even greater importance, it is strongly felt this may offer the missing key to understanding some aspects of biological behaviour. This hitherto undefined system has a structural unit which, for reasons that will be discussed, has been named an aphron. An aphron is made up of a core which is often spherical, but is not necessarily so, of an internal phase, usually liquid or gas, but not excluding solid, encapsulated in a thin aqueous shell. This shell contains surfactant molecules so positioned that they produce an effective barrier against coalescence with adjacent aphrons.

Protected by the encapsulating shell, aphrons can attract one another to build up complex aggregates, but unlike the attraction between individual molecules, which is due to van der Waals forces, the attractive force between aphrons is largely due to surface forces. Surface forces have essentially the same origin as van der Waals forces, albeit expressed in a different way, but have the added property that they change with changes of concentration and ionic strength. These introduce additional controls which confer unusual properties

on aggregates of aphrons, particularly those which have a liquid in the core. It will be shown towards the end of the book that many biological mysteries could be explained because of this.

It is unfortunate that interfacial phenomena have not been given adequate coverage in undergraduate chemistry courses. Some otherwise excellent texts have omitted the subject entirely. For that reason many readers would not be properly prepared to understand the basic principles which are essential for an appreciation of the subject matter of this book, and this deficiency has to be remedied in the early chapters. Furthermore, this book is not intended for chemists alone. Surfaces play some role in almost all science disciplines, and there is material in this book which would be appropriate to those working in the fields of chemistry, physics, geology, cell biology, and many branches of engineering including chemical, materials, aerospace, mechanical, civil, sanitary and environmental engineering. It would be of interest to those working in soil science, textiles, medicine and pharmacy, and there is even a chapter which could be of interest to artists. In other words, this is an interdisciplinary book, of which there are relatively few, and in a subtle way it emphasizes that scientists have, perhaps, gone too far along the road of specialization and it is time to bridge the artificial fences of compartmentalization that have been erected largely for intellectual convenience.

Catering for such a diverse readership introduces restraints on the contents and it determines what the book cannot and does not pretend to be, namely a definitive monograph on the liquid-fluid interfaces. Rather, it will attempt to cater for those who have an interest in the topic but have had little contact with the fundamentals of science of fluid surfaces. In this way it will aim at achieving two objectives. Firstly it is hoped that this book will stimulate an interest in the many applications of surface activity, and perhaps induce the reader to delve further in the field, and secondly, it is hoped that there will be enough background covered for the reader to appreciate the subject matter developed in the book. It is intended that it will be self-consistent and simply written, so that the first chapters could provide material for an introductory few lectures on the subject which could be given in departments other than chemistry. The mathematics that is introduced is the minimum required and is of an elementary level. References are reduced to a minimum. Above all, it is hoped that the fascinating material, much of which is new, will provide sufficient enthusiasm for the reader to continue

studying in the area and, if he be research orientated, enter the field himself. It is still virtually unexplored territory.

Chapters 2 and 3 are designed to provide the reader with the basic fundamentals related to fluid interfaces. The interfacial phenomena related to the liquid–gas and liquid–liquid interfaces are discussed, as well as the properties associated with thin aqueous films, an area rarely introduced in undergraduate studies. The next chapter deals with the structure of giant gas core aphrons, which are familiar to most as simple bubbles of the type children blow through a pipe, as well as their aggregates, which are simply conventional foams. Their stability and properties are reviewed in the light of surface forces and thin film behaviour. The fifth chapter moves to the novel system, colloidal gas aphrons, where new features become predominant because the bubbles are micron-sized and so exhibit colloidal properties. The unusual property of this system is that it is flowable and for that reason it is suitable for controlled industrial application.

Chapter 6 discusses thin films of oil spread on water, more familiar as oil-slicks, and the changes introduced when there is a surfactant dissolved in the water. This behaviour is not well documented, and an understanding of this is essential before the behaviour of oil-core aphrons can be discussed. The spontaneous movement engendered in such systems is described and interpreted on the basis of surface tension gradients. The next chapter deals with the properties of biliquid foams, a system unheard of fifteen years ago, but one of great significance, although they are simply foams with the gas in the cells replaced by a liquid which is virtually immiscible with water. This leads into Chapter 8, which discusses the properties of those biliquid foams where the units are of micron or submicron size. These still have some of the properties of foams, but are of very much greater stability. There can be as much as 96% of oil dispersed in 4% water as the continuous phase, and because of the new properties introduced by the small size of the units they have been given a special name, and are known as polyaphrons. They are structured liquids, clearly distinct from liquid crystals, with flow characteristics which are non-Newtonian, but easily manageable. Polyaphrons can be considered as ordered liquids, although the units that are ordered are not molecules but oil-core aphrons.

Chapter 9 is a brief review of applications of bubbles (perhaps better referred to as gas cavities) to separations in some well-known flotation techniques. Chapter 10 deals with possible applications of colloidal gas aphrons (CGA). These applications are considerably

more extensive than those dealt with in Chapter 9, because CGAs can be generated at one place and transferred through a pipe to the place of application. Chapter 11 discusses some of the applications of polyaphrons. These include separations, detergency and use as fuels. Chapter 12 serves only as an introduction to the concept of invert aphrons as there is not as yet much information available. Invert aphrons appear to consist of minute water globules, also encapsulated by a soap film, but further strengthened by a shell of very much smaller oil-core aphrons. Such systems may also be more prevalent than has been realized and may be very significant in cellular structures and behaviour.

Chapter 13 is also very short and is intended to draw attention to the possibility of producing aphrons with a solid core, as well as some unusual types of aphron. Chapters 14 and 15 unify the aphron concepts in relation to biological phenomena, showing how many problems related to intercellular and intracellular behaviour become more understandable if the hypothesis is made that the granules present in cells are, in fact, structured as aphrons. After discussions of biomembranes and cancer, which are certain to be controversial, it will be somewhat of a relief to get to the final chapter which is designed to show that science can have its fun side, and the experimental facts discussed in the earlier chapters can be used in a relaxing new art form called 'painting on water'. This is very easy to do, and the patterns so produced are unique and very beautiful. It is possible to fix them permanently, and the resulting pictures have some of the beauty of stained glass, but have in addition the appearance of movement which is lacking in stained glass.

If there is a single thread which can be said to unify this book it is the importance of surface tension in so many diverse areas. This arises for two reasons. Firstly, in most of the systems discussed water is an essential component, and water has the highest surface tension of all non-metal liquids. Secondly, the surface tension of dilute aqueous solutions is very sensitive to the concentration of some solutes, so variations of surface tension, and therefore of the forces available due to surface tension, can occur at different places in the system. This introduces considerable flexibility. Arising out of this is the ability of surface tension forces to be converted into movement, and much of the experimental evidence to be presented involves such movement. This cannot be adequately conveyed in a static drawing or photograph. Much of this evidence has been recorded on video-

tape, but it is still just a little too early for a videocassette to form part of this book.

Where appropriate, details are given so that these experiments can be reproduced. The equipment needed is very simple—either a transparent baking dish or a simple microscope. It is hoped that readers will take the time to repeat some of these experiments themselves. The results will be very rewarding. If the baking dish is placed on the stage of an overhead projector, some fascinating lecture demonstrations can be provided which are appreciated by school children and learned professors alike. The author has a 15-minute videotape entitled 'The Life and Loves of Amy the Amorous Amoeba', which is always well received, and something like this can easily be improvised on the overhead projector, once the basic principles outlined in this book have been understood.

In composing this book it was found desirable to invent several new words. Undoubtedly, there will be some who will complain about this, but in fact this was done in order to define more clearly the different systems that can occur, and in this way make the distinctions more understandable. The definition of two-phase liquid systems under the umbrella term 'emulsions' has delayed a proper appreciation of the many different arrangements that can occur. It is hoped that by drawing distinctions through the use of new terms it will become easier to understand multiple-phase fluid systems. After all, that is the proper function of words.

Criticism may be voiced that there is much in this book that is speculative and therefore controversial, but no apology is offered for this. When new frontiers are opened up, speculation is justified as a stimulus to others. It would take many workers and many years of effort to answer all the questions opened up by the aphron concept, and the author feels he has a responsibility to the scientific community to explain the many avenues for research and development of which he is aware. Undoubtedly there are many more which will occur to the reader. Should that be the case the author will feel that he has been amply rewarded.

CHAPTER 2

Forces Operating at Interfaces

Intermolecular Forces

In the final analysis, all the forces that operate between molecules are electrical in origin and depend upon the electronic nature of the structure of all atoms, with a positively charged nucleus at the centre and the negatively charged electrons peripheral. If the molecule is such that there is a permanent displacement of balance of charge so that one part carries more negative charge and correspondingly another part is more positive, then the molecule is polar, behaving like a small dipole, having a dipole moment which is a product of the charges and the distance separating them. Such dipoles can attract one another and, given the opportunity, will orientate themselves, aligning up so that the negative end of one is near the positive end of its neighbour. This orientation is disturbed by the movement of the molecules, due to the thermal energy for which temperature is the measure. Water, because it is a small molecule and contains the highly electronegative oxygen atom, shows this attractive force to a marked extent, the positive part of the dipole being centred between the hydrogen atoms. In addition, because of the electropositive nature of the hydrogen atom and the very small size of the proton, which is the residue left when the hydrogen atom loses its electron, hydrogen bonding exists in liquid water even when its temperature is raised to the boiling point.

London Forces

However, even molecules which are not themselves dipoles attract one another. The forces responsible are known as London or dispersion forces. They originate because any atom can be considered as a fluctuating dipole due to the positive charge at the centre with negative electrons moving very rapidly around it. If an instantaneous

photograph of an atom could be taken so that the electrons could be frozen in position, there would be a resultant dipole made up of all the dipoles created by every negative electron and the pivotal positive nucleus. Such a dipole will induce a dipole in a neighbouring atom and the two will interact because of the resultant attractive force just as do molecular dipoles. However, these will be ever-changing dipoles, sometimes referred to as oscillating dipoles, because of the very rapid movement of the electrons, but the overall effect is to produce an attractive force, which is inversely proportional to the sixth power of the distance between the atoms. Clearly the more electrons and the higher the charges on the nuclei, the greater will be the cumulative attractive force of these London forces. For that reason the higher the atomic number of the atoms or the molecular weight of molecules, the larger the London forces will be. The combined effect of London forces and any dipole-dipole attractions produces the attractive forces usually known as van der Waals attractions. As they fall off rapidly with distance apart, because of the sixth power relationship, they are known as short-range van der Waals forces. It will be shown later that there are also long-range van der Waals forces which play a very important part in colloidal phenomena.

It is these forces which are responsible for the liquefaction of gases at temperatures below the critical temperature. This is the temperature above which liquefaction of a specific gas cannot occur no matter how high the pressure. Because of their movement, molecules of a gas possess kinetic energy equal to $\frac{3}{2} \times kT$, where k is the Boltzmann constant ($= 1.38 \times 10^{-23}$ J/deg/molecule) and T is the temperature in kelvins. This energy tends to be disruptive, and because it is related to the entropy, which, effectively, is this energy divided by the temperature in kelvins, it can be called the entropic effect. It represents the energy tending to separate the molecules and thus increase the degree of disorder.

In opposition to these forces there are the attractive van der Waals forces which tend to pull the molecules together, thus establishing some degree of order. It is, therefore, appropriate to term this energy enthalpic, because the energy needed to overcome this attraction at constant pressure is one of the forms of energy generally known as the enthalpy. If the pressure is raised, the effect of these forces increases because the molecules approach one another. At the critical temperature and pressure, the disruptive kinetic energy is just balanced by the attractive van der Waals forces. If either the temperature is decreased or the pressure increased, at a temperature

which is just below the critical temperature and pressure, the gas will liquefy. This statement simply means that, on average, below the critical temperature most of the molecules will no longer have enough energy to vaporize and leave the crowded liquid state.

Forces at Surfaces

Because the gas and liquid states are indistinguishable at the critical state, there is no surface possible, but just below the critical temperature there will be a distinct surface separating gas from liquid. In the critical state the density of gas and liquid must be the same but below the critical temperature the liquid will be denser than the gas and, therefore, will have different optical properties, so a clear surface separating the liquid from the gas becomes visible. However, there will always be some vapour because there will always be some molecules with enough kinetic energy to escape from the liquid. These will be relatively few so that the vapour in equilibrium with the liquid will have a markedly lower density. It is possible to calculate the density of molecules on either side of the interface. For example, at 20 °C, the density of water is 0.998 g/cm³, from which it can be calculated that the number of molecules on the surface of the water would be 1.05×10^{15} /cm². On the other hand, the density of water vapour at the same temperature at its vapour pressure would be 1.7×10^{-4} g/cm³, which would give a density of number of molecules on the surface of 3.2×10^{12} /cm², very much less than that in the liquid.

Using this number, it is calculable that the average distance between the molecules in the liquid surface is 0.31 nm, and on the vapour side it would be 5.6 nm. If the van der Waals forces are taken as being inversely proportional to the sixth power of the distance between the molecules, the relative attraction between molecules in the liquid state to the attraction between molecules in the gaseous state would be 3.5×10^7 , or approximately thirty million times more. The net effect of this is to produce a force pulling the molecules at the surface of the liquid inwards. This force is known as the *surface tension*.

Surface tension, for which the symbol γ will be used, can be defined as the force needed to split a liquid surface, completely apart, along a line which is 1 cm in length, and it is therefore expressed in units of force/cm. Sometimes, however, it is preferable to define the property in terms of surface energy/unit area, which is the work