Molecular Adhesion and Its Applications

The Sticky Universe

Kevin Kendall

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I wish I could derive all phenomena of nature, by some kind of reasoning, from mechanical principles; for I have many reasons to suspect that they all depend on certain forces by which the particles of bodies are either mutually attracted and cohere in regular figures or are repelled and recede from each other

I. NEWTON, 1687

FOREWORD

At the beginning of the twentieth century, engineers and technologists would have recognized the importance of adhesion in two main aspects: First, in the display of friction between surfaces—at the time a topic of growing importance to engineers; the second in crafts requiring the joining of materials—principally wood—to form engineering structures. While physical scientists would have admitted the adhesive properties of glues, gels, and certain pastes, they regarded them as materials of uncertain formulation, too impure to be amenable to precise experiment. Biological scientists were aware also of adhesive phenomena, but the science was supported by documentation rather than understanding.

By the end of the century, adhesion and adhesives were playing a crucial and deliberate role in the formulation of materials, in the design and manufacture of engineering structures without weakening rivets or pins, and in the use of thin sections and intricate shapes. Miniaturization down to the micro- and now to the nano-level of mechanical, electrical, electronic, and optical devices relied heavily on the understanding and the technology of adhesion. For most of the century, physical scientists were aware that the states of matter, whether gas, liquid, or solid, were determined by the competition between thermal energy and intermolecular binding forces. Then the solid state had to be differentiated into crystals, amorphous glasses, metals, etc., so the importance of the molecular attractions in determining stiffness and strength became clearer. Cross-linked rubbers and composites designed at the macro- and micro-level were developed to extend the range of materials available for engineering purposes. Adhesion at the molecular scale, at surfaces and interfaces, was recognized to be a vital factor determining performance.

Biological sciences were not excluded from this explosion of knowledge. The study of cell structure and cell behavior, including material transport across membranes, cell division, and cell adhesion, raised aspects of adhesion already familiar in physical colloid systems. Then the rise of molecular biology in the last

30 years has brought adhesion into prominence at all levels of organization in biological systems.

Certainly there is a vast literature, and especially a voluminous research canon, associated with the science of adhesion. However, the literature is fragmented and diffuse because adhesion is involved in all areas of endeavor. The engineering literature is somewhat more ordered because of the need to agree good practice and safety protocol. It is nevertheless compartmentalized. Even so, it is not easy to align scientific knowledge with engineering practice in many fields of application. One possible exception is computer modeling, which is at the cutting edge of advances both in science and engineering though the emphasis is rather different. No doubt, in the future, we shall see adhesion modeled at the molecular level and tracked through to engineering practice with the aid of computers.

Remarkably, there is no scientific monograph covering the state and current knowledge of adhesion. Nor is there an engineering treatise to take the reader onto a representative range of applications. This is not because we have lacked leading scientists or engineers or gifted teachers in the twentieth century. Presumably, they have been too busy in a field of rapid progress. Now the challenge of promoting a unified account of molecular adhesion, extending it to basic laws and technical practice and onto applications has been taken up by Kevin Kendall. His enthusiasm for the subject and his experience in academe and industry shines through this comprehensive treatise. It is a book that can be read from cover to cover, or a laboratory and design manual to be dipped into as work demands. It benefits enormously from the distillation of a vast subject through a single mind.

Sir Geoffrey Allen FRS

PREFACE

Molecular adhesion is one of the most fundamental concepts in science. Molecules tend to be stuck together to form crystals, liquids, composite materials, assembled structures, colloids, rocks, pastes, living cellular creatures, and so forth. Our universe may be expanding against the force of gravity, but each local bit of the universe is firmly stuck together by molecular adhesion. Explaining this across the interdisciplinary boundaries of chemistry, physics, engineering, and bioscience is the objective of this book. The argument is at undergraduate teaching level, but the specific examples and references are geared for research specialists.

The laws we remember from school are the laws of motion. Movement is interesting whereas stasis is boring. Newton made the gravitational law of adhesion exciting by using it to explain the movement of planets and satellites. Yet our Earth is largely static; stuck together by molecular adhesion. Our bodies lie in the tenuous skin of mobile material at the Earth's surface, which explains our fascination with movement, leading to Newton's Laws of Motion. To suggest laws of adhesion is almost a joke, rather like one of those Andy Warhol movies where nothing happens. But molecular adhesion is interesting precisely because it limits the movement we want; the movement of a car on a road, the movement of cornflakes onto our plates. Laws of adhesion must exist and should be revealed. Four centuries ago, Galileo famously said "It moves"; this century we are saying "It sticks".

Previously, we could only detect adhesion by this limit of movement. The single way to test for adhesion was by breaking the bond. Now nondestructive tests are becoming possible using the new technique of atomic force microscopy at the molecular level. Thus adhesion can be distinguished from, then related to, fracture. We have to understand both making the joint and breaking it to obtain a rational picture of adhesion as a whole. A second major advance is in computer modeling which enables us to describe the interactions of the many thousands of atoms which participate in adhesion events. Adhesion is cooperative; the adhesion of 1000 atoms is different from the adhesion of 1 atom.

Roughly 6000 articles are written each year on adhesion but these are in widely varying disciplines which may not be immediately accessible. This book cannot quote all these papers, nor can it present a comprehensive critique of the documents, but it can provide a skeleton of logic and a common agreed language for describing adhesion phenomena in those different areas, together with an assessment of the pivotal contributions in the literature. Individual researchers should find, in the framework provided here, a place to fit their own observations.

Many books on surface chemistry contain a short chapter on adhesion. But such accounts are seldom satisfactory. Clearly, adhesion stems from the strong attractive forces between molecules. However, the connections between molecular forces and phenomena seen in soiling, cements, adhesives, corrosion, catalysis, or slime mold reproduction are not normally made explicit. Similarly, there are several texts on adhesion for engineers, though most engineers, following Coulomb and Hertz, have ignored adhesion. In a typical book on Contact Mechanics, only 1% deals with adhesion. Engineering books tend to be dominated by mathematical derivations and hardly acknowledge that molecules exist. But without molecular force, there is no adhesion. In this book I have emphasized the observations of phenomena based on adhesion, keeping the mathematical description to a minimum, concentrating on useful results rather than analytical manipulations, trying to show the connection between molecules and mechanics.

The book is in three parts. The first introduces the background and lays the fundamental tenets of the subject which really go back to Isaac Newton. He experimented on the contact of glass lenses, trying to interpret the results in terms of molecular adhesion long before the idea of molecules existed. The second part of the book seeks to establish the laws and mechanisms of adhesion, and the third to explain the applications and benefits of molecular adhesion in the practical world.

In the first part, the aim is to unravel the many ideas and theories which have been proposed to account for adhesion phenomena, to pin down the key observations which have led to our current state of thinking, and to establish three "laws of adhesion" which account for the phenomenology. The second part then goes on to establish the three laws on a more quantitative and theoretical level which can be tested by new theories of computer modeling and by new measurements such as Atomic Force Microscopy. Finally, in the third part, this theory of molecular adhesion is applied to eight important areas of technology, where the effects of intermolecular forces are dominant. These areas will be familiar in most industries. They include adhesion of particles, colloids, pastes, gels and cells, the adhesion of nanomaterials, of films and coatings, the fracture of adhesive joints, and composite materials. A concluding chapter points to the future of molecular adhesion science.

My hope is that the adhesive gulf between chemists, engineers, and biologists can be joined, while simultaneously helping those materials scientists, dentists, powder technologists, cancer specialists, etc., who are fascinated by adhesion effects. If so, thanks are due to my wife for her constant support, to Professor Mai for allowing me to work in his department on a sabbatical in 1997, to Professor Tabor who gave me the stimulus to think about the issues in this book, and to many colleagues who have debated, theorized and experimented on this subject with me over the past 30 years. If not, please email me on k.kendall@bham.ac.uk, fax me with your comments on +44 (0) 121 414 5377, or write me at the Department of Chemical Engineering, University of Birmingham, Birmingham, UK.

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