

INTERMOLECULAR FORCES

Their Origin and Determination

By

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PREFACE

The forces between molecules are of interest to scientists in a wide range of disciplines as these interactions control the progress of molecular collisions and determine the bulk properties of matter. Some twenty-five years ago, the subject was treated comprehensively in the classic text by Hirschfelder, Curtiss, and Bird: *The molecular theory of gases and liquids*. In addition to giving a thorough account of the molecular theory of matter, much of which is still relevant at the present time, this book also attempted to reconcile the properties of matter in terms of simple intermolecular potential energy functions† such as those due to Lennard-Jones. This aspect of their book has not stood the test of time, although it was not until the 1970s that a firmer foundation to the subject could be laid. During this period a quantitative understanding of the intermolecular forces of a number of monatomic species—in particular the inert gases—was achieved and found to bear little relation to the simple functions widely employed previously. These advances have been based on a number of factors such as the development of new types of experimental measurement, new attitudes to data analysis and the availability of high-speed computers, leading to a subject very different from that described by Hirschfelder, Curtiss, and Bird. It is now important to reassess the subject of molecular interactions in the light of this transformation.

This book provides a wide-ranging account of the determination of intermolecular forces. It describes both the techniques that have been developed in recent years and the potentials that have resulted from their application. Particular attention has been paid to molecular beam scattering and the spectroscopy of van der Waals dimers, which can provide extremely detailed information about certain aspects of intermolecular potentials. A comprehensive account is also given of macroscopic, thermally averaged properties such as second virial coefficients and dilute gas transport properties, which have recently become re-established as important sources of information about intermolecular forces. Among the factors which have contributed significantly to the progress of the past ten years are an increased appreciation of the complementary nature of the information contained in these different properties and the development of more direct routes from properties to potentials. Both these aspects are emphasized strongly in this book.

In writing about intermolecular forces a certain arbitrariness in defining the boundaries of the subject is necessary. We have, for example,

† Throughout this book, these will be referred to quite simply as 'potentials'.

not included the topic of hydrogen bonding and have referred only briefly to interactions involving ionic species. Naturally, we have given most attention to those systems (mainly monatomic) where the potential is known with high accuracy and have not devoted much coverage to the many superficial attempts to deduce potential functions from either limited data or inadequate techniques. However, in the case of polyatomic molecules, even though little quantitative information is at present available, we have tried to indicate those results which should provide a basis for future progress. Traditionally, many attempts have been made to deduce pair potentials from condensed phase properties. However, as some uncertainty still surrounds the role of non-pairwise additive contributions to intermolecular energy, pair potentials are most soundly deduced from those properties which involve only pair interactions. For this reason we have given only a very general account of the use of condensed phase properties in determining pair potential functions.

It is impossible to separate the determination of intermolecular forces from an understanding of their relationship to molecular and thermophysical properties, and any book of this sort must of necessity include a considerable amount of statistical mechanics and scattering theory. To give a comprehensive account of these subjects would lead to a work of excessive length. Our practice has been to include sufficient coverage of only those aspects that are essential to an understanding of the elucidation of intermolecular forces. It should be emphasized that this is not a treatise on the fundamental theory of intermolecular forces, although one chapter has been assigned to this topic.

It is our intention that this book should prove useful to a wide variety of scientists. Some may be senior undergraduates or new graduate students who require a modern account of the fundamentals of the subject, some will be research workers directly concerned with investigating the nature of the forces between molecules, whereas others will simply wish to use the best current knowledge of the force laws to calculate the thermophysical properties of substances in which they are interested. In order to cater for such diverse interests, different sections of the book have been consciously written at several levels. A key indicating these levels is attached to the table of contents. This identifies those sections which, taken together, provide a suitable introduction for those approaching the subject for the first time, and those sections, largely theoretical, which may not be necessary for those readers more concerned with the application of the results contained in the book rather than their derivation. To this end we have felt it advisable to cover some subjects more than once to provide a fairly comprehensive treatment of the subject at each level. It is inevitable that such a format should lead to inhomogeneities in the text which may trouble those who wish to read the

book through. However, we believe that the benefits of this approach far outweigh the disadvantages.

In addition to its pedagogical role, the book is intended to be a work of reference. With this in mind, we have included a large quantity of numerical material in the text and appendices. This comprises tabulations, both of useful modern potential functions, and of the equilibrium and transport properties calculated using them. We have also given copies of computer programs which enable equilibrium and transport properties to be calculated for any given potential function. In addition, a quantity of selected experimental data is tabulated for a limited number of reference substances. After decades of relative stagnation, the field of intermolecular forces is now progressing at a rapid rate. In compiling the material in the book we have sought to emphasize those aspects of the subject which we believe to be the least ephemeral. To those building on the foundations described in this book, we would make a strong plea for extreme caution. The history of research into intermolecular forces shows that the most common pitfall has been overconfidence. Again and again workers have been too easily satisfied by superficial answers, and have chosen to ignore the limitations of their approach. We now appear to have a solidly based understanding of the forces in many monatomic systems and it is important that, as we turn to more complicated molecules, we do not expect easy results. Progress will only be made by an uncompromisingly critical approach.

The authors wish to thank their friends and colleagues for the enormous help which they have received in the preparation of this book. Their contributions are acknowledged below. We would be most grateful if readers would draw any mistakes to our attention and would be most happy to receive general comments and criticisms.

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* These sections provide a suitable introduction for readers approaching the subject for the first time.

† These sections may not be necessary for all users on a first reading.

INTRODUCTION

1.1. Historical background

The molecular theory of matter has its roots in the philosophical speculations of the atomists of the fifth century BC, Leucippus and Democritus, who suggested that all matter was composed of small, rapidly moving particles they called atoms. This idea, somewhat modified to avoid the determinism which atomists saw as a natural corollary, was incorporated by Epicurus into his wider philosophical scheme and was an important influence on Greek and Roman thought. It was expounded in a long poem *On the nature of the universe* by Lucretius,¹ a Roman Epicurean of the first century BC. Many of the features of the molecular theory described by Lucretius are in surprising accord with modern views. Matter was conserved in all processes, there was a large, but finite, number of species of atom, and the atoms moved at high speeds. The deterministic consequences of the model were avoided by allowing the atoms to 'swerve ever so little from their course' at random times and places—an ingenious precursor of the uncertainty principle. The concept of molecular interactions was also developed, but the distinction between chemical and physical forces between the atoms was of course missing.¹

Again, things that seem to be hard and stiff must be composed of deeply indented and hooked atoms and held firm by their intertangling branches. In the front of this class stand diamonds . . . Liquids on the other hand must owe their fluid consistency to component atoms that are smooth and round.

The relationship between molecular properties and the viscosity of fluids was also considered.¹

We see that wine flows through a strainer as fast as it is poured in; but sluggish oil loiters. This is no doubt either because oil consists of larger atoms or because they are hooked and intertangled and therefore cannot separate so rapidly, so as to trickle through the holes one by one.

These ideas represented the limit to which molecular theory could be developed. Further advances required new experimental information that could not be obtained from a casual inspection of the universe. Two millenia were to pass before the techniques were developed and the necessary experiments performed. From the fifteenth century new observations laid the foundation for a scientifically based dynamic molecular theory. But despite many important theoretical developments, starting with Bernoulli² in 1738, the main tenets of the modern molecular theory

of matter, in particular the idea of molecular motion in gases, were not generally accepted until the latter half of the nineteenth century. The powerful mathematical theories of Clausius, Maxwell, and Boltzmann between 1850 and 1890 brought to fruition the kinetic theory of gases.³⁻⁹ After this period it was universally recognized that temperature and pressure are both related to the motion of the molecules. The pressure is due to the force that molecules exert on the walls of a container by virtue of their collisions with the walls and temperature is a measure of the average kinetic energy of the molecules.

The idea of intermolecular forces also has a long history. The concept of molecules as point sources of attractive and repulsive forces was first formulated by Bosovich (1783). He recognized that molecules must repel each other at very small separations but assumed that the attraction and repulsion alternate a number of times as the separation increased. By the early nineteenth century the fact that molecules could repel each other was acceptable even to the advocates of the phlogiston theory of heat who regarded gaseous molecules as stationary objects held in their positions (on a lattice) by mutual repulsion. Later, the modern view that molecules repel each other at small separations and attract each other at long range became established. It was clearly stated by Clausius in 1857.

Maxwell incorporated into the description of the kinetic behaviour of gases the idea that molecules exerted forces on one another. He presumed that the forces were entirely repulsive in character and that they decayed as the separation between the interacting molecules increased. He was able to deduce the temperature dependence of the viscosity of a gas of such molecules. Boltzmann, attempting a similar calculation, invoked a series of intermolecular force laws all of which contained attractive components. It is interesting to note that his results provided an equally acceptable description of the behaviour of the viscosity of gases to that of Maxwell despite the gross differences in the assumed force law. In 1873 van der Waals developed an equation of state for a gas whose molecules were supposed to be impenetrable rigid spheres surrounded by an attractive force field. This concept enabled van der Waals¹⁰ to show that the pressure exerted by such a gas lay below that for a gas whose molecules were non-interacting points (the perfect gas) owing to the retardation effect of the attractive forces on molecules colliding with the wall. In addition, the non-zero volume of the gas molecules reduced the volume available for motion of molecular centres, below that for non-interacting points. Thus he deduced the van der Waals equation of state

$$\left(P + \frac{a}{\tilde{V}^2}\right)(\tilde{V} - b) = RT$$