

**A KINETIC THEORY  
OF GASES  
AND LIQUIDS**

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A kinetic theory of gases and liquids by Richard D. Kleeman

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# A KINETIC THEORY OF GASES AND LIQUIDS

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TO MY PARENTS**

## PREFACE

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THE object of writing this book is to formulate a Kinetic Theory of certain properties of matter, which shall apply equally well to matter in any state. The desirability of such a development need not be emphasized. The difficulty hitherto experienced in applying the results obtained in the case of the Kinetic Theory of Gases in the well-known form to liquids and intermediary states of matter has been primarily due to the difficulty of properly interpreting molecular interaction. In the case of gases this difficulty is in most part overcome by the introduction of the assumption that a molecule consists of a perfectly elastic sphere not surrounded by any field of force. But since such a state of affairs does not exist, the results obtained in the case of gases hold only in a general way, and the numerical constants involved are therefore of an indefinite nature, while in the case of dense gases and liquids this procedure does not lead to anything that is of use in explaining the facts.

Instead of an atom, or molecule, consisting of a perfectly elastic sphere, it is more likely that each may be regarded simply as a center of forces of attraction and repulsion. If the exact nature of the field of force surrounding atoms and molecules were known, it would be a definite mathematical problem to determine the resulting properties of matter. But our knowledge in this connection is at present not sufficiently extensive to permit a development of the subject along these lines. But in whatever



way the subject is developed fundamental progress will have been made only if molecular interaction is not, as is usually the case, represented by the collision of elastic spheres. It will be shown in this book that the subject may be developed to a considerable extent along sound mathematical lines yielding important results without knowing the exact nature and immediate result of molecular interaction. Thus it will be found, for example, that the definition of the free path of a molecule in connection with viscosity, conduction of heat, diffusion, etc., may be given a form in each case not involving the exact nature of molecular interaction, which is mathematically quite definite, and which therefore applies equally well to the liquid and gaseous states. Since in the gaseous state each kind of path is proportional to the volume of the gas, its interest is then mainly associated with the characteristic factor of the volume which makes the product numerically equal to the path. A direct physical meaning may be given to this factor.

In constructing a general Kinetic Theory the problem that presents itself first for investigation is the dependence of the velocity of translation of a molecule in a substance on its density and temperature. It is often assumed that this velocity is the same in the liquid as in the gaseous state at the same temperature. It can be shown, however, that this holds only for each molecule at the instant it passes through a point in the substance at which the forces of the surrounding molecules neutralize each other. The total average velocity corresponding to the whole path of a molecule is usually much greater than the foregoing velocity in a liquid and dense gas on account of the effect of the molecular forces of attraction and repulsion.

The pressure which the molecules exert tending to expand the substance, or the expansion pressure, and the number of molecules crossing an area of one square centimeter from one side to the other per second, evidently depend on the

magnitude of the total average velocity. It can be shown that if the molecules have no apparent volume, or no volume associated with each molecule through which another molecule cannot pass, the expansion pressure is equal to the number of molecules crossing a square centimeter per second multiplied by a factor whose value is the same as if the substance were in the perfectly gaseous state at the same temperature and density. The apparent molecular volume of the molecules may be defined as the quantity whose change in magnitude at constant temperature and density would not affect the total average velocity. Its definition is thus mathematically definite. The effect of this quantity on the expansion pressure is to increase it in the ratio of the volume of the substance to the difference between the volume and the apparent molecular volume. The expansion pressure of a substance is evidently balanced by the sum of the external pressure and the intrinsic or negative pressure due to the attraction of the molecules upon each other, the equation expressing this relationship being a form of the equation of state.

In the case of a mixture it is convenient to introduce the terms "partial expansion pressure," "partial intrinsic pressure," and "partial external pressure," in connection with each constituent. Each partial expansion pressure is balanced by the sum of the corresponding partial intrinsic and partial external pressures, similarly as in the case of a pure substance. The property of osmotic pressure can then be shown to be a function of the corresponding partial intrinsic pressure of the mixture, and the number of molecules giving rise to the osmotic pressure which cross a square centimeter from one side to the other per second. This is what we would expect, since osmotic pressure must be the outcome of the fundamental properties of a substance—the motion of translation of its molecules, and the forces they exert upon each other.

With the foregoing results as a basis, and the modified definitions of the free paths of a molecule mentioned, the foundation of a general Kinetic Theory can be laid which applies to matter in any state, and which furnishes a number of important formulæ. These formulæ may be given important extended forms containing quantities which are arbitrary in so far as they satisfy the formulæ as a whole. Formulæ may also be deduced along the same lines involving instead of the molecular free path the projection of the motion of a molecule along a line. This projection and its period are also arbitrary in so far as they satisfy the formulæ as a whole. Some of them find an interesting application in connection with colloidal solutions. The foundation of the subject may be said to be fairly complete, since it furnishes the structure about which further advances may be made so that the subject can be rendered more or less complete. These advances will consist largely in expressing the constants involved in the fundamental formulæ in terms of the constants of the molecular forces and the molecular volume. If the formulæ obtained in connection with viscosity, conduction of heat, and diffusion, be applied to a perfect gas, they assume the well-known forms, but the symbols have somewhat different meanings.

The development presented is perfectly sound without involving difficult mathematics. This has, in fact, been one of the main objects kept in view. As a physicist I have often failed to see the usefulness from a physical standpoint of the extremely intricate mathematical investigations purporting to work out to the utmost limit the results of certain assumptions (usually in connection with molecular collision), and which have usually led to results whose usefulness seems incommensurate with the labor involved, seeing that the assumptions are usually not likely to be true. It is desirable that there should be a simple and clearcut connection between