

THE INTERNATIONAL RESEARCH CONFERENCE ON TRANSPORT PROPERTIES AND MOLECULAR FORCES*

Transport properties are the coefficients relating fluxes of molecular properties (such as mass, momentum, and energy) to gradients of macroscopic variables (such as density, fluid velocity, and temperature). The kinetic theory of gases, to the extent that it dealt with these properties, had been worked out by Boltzmann, Maxwell, Chapman, and Enskog many years ago and had to be redeveloped to describe gases of polyatomic molecules. This summary of a recent conference on gas transport properties describes some of the theoretical and experimental aspects of the recently redeveloped theory.

In fluids, the rate of transport of measurable quantities such as heat, momentum, or molecular concentration is related to the degree of imbalance of these quantities. This imbalance can take the form of a concentration, or temperature gradient, or a shear flow. As one can gather from the title, the main emphasis of the conference lay in the functional dependence of transport properties of gases on intermolecular forces between colliding atoms and molecules. As a corollary, the inverse problem of inferring those forces from macroscopic experimental data was also discussed.

This dual goal was already implicit in the classic monograph published in 1954, *The Molecular Theory of Gases and Liquids*, by J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird,¹ often referred to fondly as the Green Bible. At the time of its publication, gas kinetic theory had been worked out for structureless point-like particles interacting via short-range central field forces. As a believable approximation, it can only describe the noble gases (helium, neon, etc.) and their mixtures at temperatures below 1000 K. The extension of kinetic theory to molecules with internal structure (water vapor, for example), implying asymmetric force fields, has been actively worked during the last 30 years and now has come to the stage where it can address the same questions for polyatomic gases that at the start of this period could be answered unambiguously only for noble gases—hence, the occasion for this conference.

The site of the conference, the Theoretical Chemistry Institute at the University of Wisconsin, although not centrally located as far as the attendees were concerned, was particularly apt because it is the

institutional home of Professors Hirschfelder, Curtiss, and Bird, many of whose students have gone on to make fundamental contributions to this field. Several of their students eventually came to the Applied Physics Laboratory, and one, Dr. F. T. McClure, became chairman of the Research Center and an associate director of the Laboratory.

The association of APL and the Theoretical Chemistry Institute was in fact even closer: APL took a great interest in and supported financially the work leading up to the publication of *The Molecular Theory of Gases and Liquids*. This interest in transport theory came about quite naturally. Transport properties such as diffusion coefficients and thermal conductivities are crucial factors in flame propagation, one of the quantities one uses in predicting the performance of ramjet or rocket engines. This interest led to a research effort at APL starting with the measurements of thermal conductivities and diffusion coefficients by R. E. Walker, A. A. Westenberg, and N. deHaas and extending to my interest, working with several postdoctoral fellows and many outside collaborators, in the kinetic theory of polyatomic gases.

The kinetic theory of gases as developed in *The Molecular Theory of Gases and Liquids* is based on a simple physical picture. Structureless particles, well-defined in position and momentum, travel undisturbed most of the time but collide with each other from time to time. The collisions are considered to take place instantaneously in a small region of space and are completely described by the differential scattering cross section; this describes the distribution in space of the trajectories of the particles emerging from the collision. This is a classical picture, but it is accurate to a high degree if the wave packets describing the motion of the particles are sufficiently localized and also hang together for a time that is long with respect to the time between collisions. These conditions can be satisfied for the noble gases at moderate pressures and temperatures, and even at very low temperatures if the scattering is quantum mechanically calculated. Another simplification occurs for noble gases because they interact via central field forces. This means that the dynamical equations separate into a set of one-dimensional differential equations that are inexpensively solved on a computer. When computers became readily available 25

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years ago, a wave of papers rapidly appeared reporting calculations of transport properties of noble-gas-type molecules with varying assumptions for the central field force.

But polyatomic molecules, or molecules with internal structure, do not interact with spherically symmetric central field forces. They generally have a nonspherical shape or interact by means of asymmetric forces. If they are vibrating or rotating, the forces may not be scalar but may depend on the initial and final states of a collision. If the Born-Oppenheimer separation breaks down (i.e., if the electronic motion cannot be regarded as occurring independently of the nuclear motion) the forces may not even be local. All this had as a consequence that the equations describing collision dynamics do not separate into distinctly independent modes of motion. Thus, the dynamics calculations that were feasible 25 years ago for monatomic substances are only now becoming so for polyatomic molecules. This was a practical difficulty in the development of the kinetic theory of polyatomic molecules and led to a sizable effort in developing efficient methods of solving the quantum scattering equations and accurate, more easily calculable approximations to the solutions. Several papers at the conference were devoted to this one strand making up the total of the several efforts to extend the theory.

There is, however, another more fundamental difficulty. A well-localized wave packet (see Fig. 1) colliding at time t will form scattered waves that will travel out with different speeds depending on whether a change in internal energy in the molecule has taken place during the collisions. If the spacing

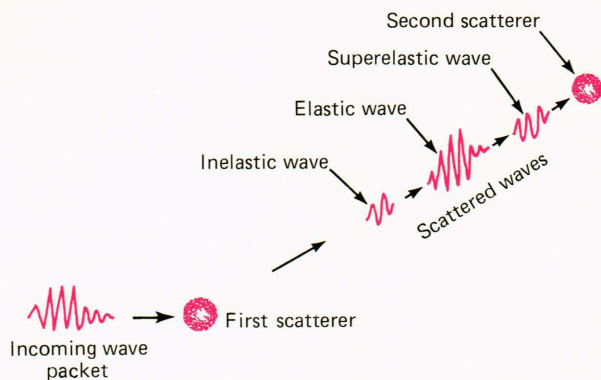


Figure 1 — A schematic of a sequence of collisions of a molecule with internal degrees of freedom with other molecules in the gas. On the left is pictured the wave amplitude of a wave packet with sufficiently narrow dispersion to satisfy a particle description; however, the distribution in internal space is not depicted. The packet is just about to collide with a target. After a time comparable to the mean free flight time, the scattered packet is about to collide with a second target. If the energy levels of the internal state are sufficiently well separated, the wave amplitudes of the states after collision will be sufficiently separated in position space to make interference effects between the wavelets negligible. This enables one to use a particle kinetic theory much like the classical theory developed by Maxwell and Boltzmann.

between the wavelets is larger than the extent of the wavelets, i.e., if

$$\Delta x_s = \frac{v\hbar}{|\Delta E_{int}|} \gg \Delta x_w = \frac{\hbar}{\langle \Delta P \rangle},$$

where Δx_s is the distance between collisions, v is the particle velocity, \hbar is Planck's constant, ΔE_{int} is the range of the energies corresponding to $\langle \Delta P \rangle$, and $\langle \Delta P \rangle$ is the range of momenta required in a wave packet to narrow it to extent Δx_w , the width of the wave packet, then this relation can be satisfied under almost all conditions for changes in energy of nondegenerate states. As soon as the possibility of degeneracy appears (i.e., where the spacing between states becomes very small), this relation cannot be satisfied. It cannot be satisfied, for instance, for the quantized orientations of any molecular rotational state (see Fig. 2). As a consequence, the wavelets striking a second scatterer may now interfere and the particle picture breaks down.

The task of accounting for these new interference effects was taken up by the late Ludwig Waldmann² of Erlangen and R. F. Snider³ of Vancouver and their students. The formal part of the theory was completed quite early,⁴ including the formal dependency of transport properties on intermolecular forces and internal degrees of freedom. Of the latter, the rotational degrees of freedom are most important because an asymmetric target that is spinning or rotating can be polarized by an asymmetric flow field—for instance, flows with shear or heat flow. This polarization or asymmetric distribution of orientations of the plane of rotation can, in turn, be de-

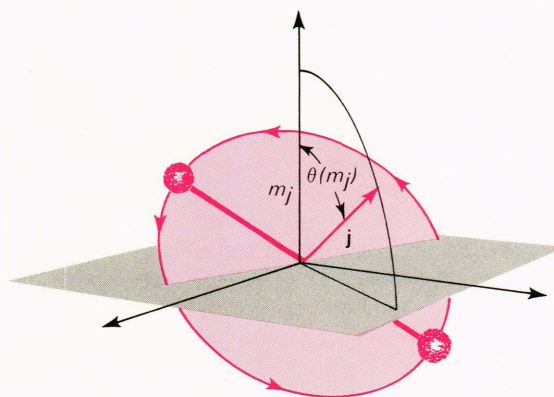


Figure 2 — A linear molecule, idealized as a rigid dumbbell, is rotating in a plane. The axis of the rotation coincides with the vector \mathbf{j} , which is the principal quantum number of a rigid diatomic molecule and which defines the total rotational energy. The magnetic quantum number, m_j , is an integer taking all values between $-j$ and $+j$. The orientation of the plane of rotation of the molecule is thus also quantized through the relation $\theta = \cos^{-1}(m_j/j)$. In an inhomogeneous flow field, the orientations of the plane of rotation will also be distributed inhomogeneously; i.e., not all values of m_j are equally probable.

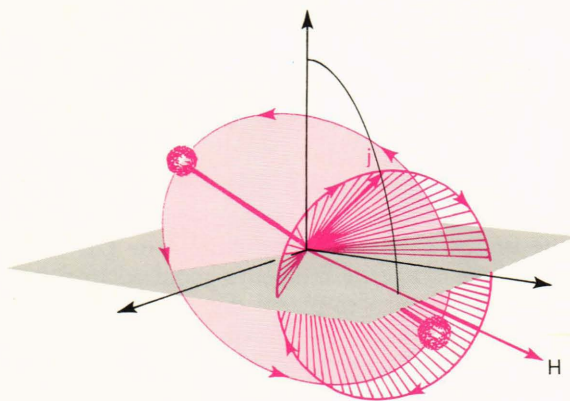


Figure 3 — All molecules have a diamagnetic susceptibility. As a result, the imposition of a magnetic field causes the end of the vector j to precess about the direction defined by H . This changes the distribution of the orientations of the plane of rotation. Experimentally, this is seen as a small change in the transport property.

stroyed by a magnetic field oriented in the right direction (see Fig. 3). A typical experimental setup would consist of a Wheatstone bridge arrangement of cells in which some property of the gas, such as thermal conductivity or viscosity, is measured. A magnetic field imposed on one leg of the bridge produces a small imbalance that can be measured with a high degree of accuracy. The observed small change in a transport property, now known as a Senftleben-Beenakker effect, had been measured in a number of elegant experiments carried out by Prof. Beenakker's group at the University of Leiden.⁴

At the conference, it became apparent that the field had progressed to the point where the main questions that were being asked were as follows: What are the limitations of the theory in its present state? What have been its main achievements? How close are we to calculating an observable for any arbitrary molecular system? How much do the experimental data tell us about molecular parameters? The first question was addressed by R. F. Snider, who summarized the fundamental basis of the present theory (which is based, as we have seen, on a localized particle picture) and the criteria for determining when it is applicable. The chief of these seems to be that the frequency of collisions should be much greater than the natural rate of change of the quantum phase of the system, i.e., when the wave packets do not disperse between collisions. The present theory is not adequate, for instance, for the description of line broadening.

Another annoying fault of the present theory is that we have not been able to show that the classical limit of $\hbar \rightarrow 0$ is the theory that one would derive with completely classical dynamics of asymmetric molecules. Prof. Curtiss bypassed this by demonstrating that transport properties calculated with his classical theory are identical with those calculated from Waldmann and Snider's theory in the limit $\hbar \rightarrow 0$.

Prof. Beenakker's talk, which set the tone of the conference, primarily addressed the second question. A good part of the reason for the success of the experimental effort of his group was a close collaboration with the theoretical group at Erlangen, under the direction of Prof. Waldmann. As a result of this collaboration, one can point out four tasks that the theory can now handle more or less adequately. In the first place, it has helped tremendously with data reduction in that it predicts field dependence and types of tensor polarization that may be encountered. Since this is deduced mainly by symmetry arguments, it is the most general of the results. Next, the theory has provided integral expressions for all the macroscopic observables; these formulas have frequently revealed unexpected relationships among some of the measured transport properties and thus have helped to explain trends in experimental data. Further, it has provided formulas to relate experimental data to molecular interactions. In the last place, each transport property and its magnetic field dependence provides a potentially different "window" on molecular forces.

The implementation of the last two tasks requires detailed dynamic calculations. Since these can be expensive and involved, many approximate methods have been tried. Some of these take the form of the classical dynamics formulations of Curtiss and his students or the search for a transformation of coordinates in which the quantum mechanical scattering equations almost separate. The most successful effort along this line has been the collaboration of groups at the University of Houston, the University of Iowa, and Columbia University and briefly at APL. Reports on this effort were given by D. K. Hoffman of Iowa and A. E. Dickinson of the University of Newcastle-upon-Tyne, England. Although this transformation is now being applied by groups at the Universities of Houston, Newcastle-upon-Tyne, and Waterloo-Ontario to the calculation of Senftleben-Beenakker effects, the results so far are inconclusive.

The only successful correlations with experiment have been carried out for hydrogen at low temperatures, where exact calculations could be done at a manageable cost. This program was begun at APL with the calculation of viscosity differences of ortho- and para-hydrogen with an empirical H_2-H_2 potential energy of interaction.^{5,6} At the Max-Planck Institute at Munich these efforts were repeated and extended with a completely theoretical expression for the intermolecular interaction.⁷ In the latest development along this line, Köhler and Schäfer⁸ modified this potential and calculated a number of cross sections derivable from the field-dependent transport properties. The results were in almost exact agreement with a set of measurements of Beenakker's group on para-hydrogen. Since no approximations had been introduced into the scattering calculations, this was essentially a test of the accuracy of the model for the intermolecular forces and of the Waldmann-

Snider theory. Unfortunately, the molecular system was rather simple; to carry out similar calculations for slightly more complicated molecules would tax even the modern supercomputers. The reason for this is that the computational effort increases, for these problems, with the sixth power of the temperature or moment of inertia. The University of London has acquired an older model CRAY computer and may start attacking these calculations head-on.

The last and most interesting part of Beenakker's talk concerned the last point cited above, i.e., that each type of polarization effect measured "opens up a different window" on the molecular forces involved. Unfortunately, in the theory of gas transport properties, no elegant inversion method exists to extract a molecular force from a set of experimental data. James Clerk Maxwell was the first to attack this problem; his method consisted merely of choosing a simple analytic form for the potential with a small number of adjustable parameters. Successive adjustments of the parameters and recalculations of the scattering dynamics and of the transport properties, until a satisfactory fit is attained with experiment, are still the methods for inverting polyatomic gas transport property data. It is essentially the method used by Köhler and Schäfer in the para-hydrogen calculations.⁸

Since these are the only exact calculations carried out for a range of transport properties directly dependent on molecular asymmetry, they constitute the only answer to the last question exercising the conferees: What molecular information do these properties embody? The answer implied by the Köhler-Schäfer calculations seems to be that it is mostly the short-range components of the anisotropic molecular force field that are sensed by the magnetic components of transport properties and that many of these pieces of experimental data may be redundant as far as their force field dependence is concerned.

In place of a rigorous mathematical inversion procedure, a recipe has been developed for speeding up

the rate of convergence of the successive approximation scheme described in the last paragraph. This recipe, developed at Oxford, London, and Brown University, so far has only been worked out for noble gases. It seems to find a path of steepest descent to the force model in best agreement with the experiment, but the procedure cannot be, or has not been, justified by any mathematical analysis. As such, it affords an empirical "sensitivity analysis," a term well known to engineers if not to physicists, for assessing the dependence of transport properties on molecular models. A group at Princeton is, in fact, working out a mathematically respectable "sensitivity analysis" to be applied to polyatomic gas properties. It may only be simple justice that, whereas engineers have looked to chemists and physicists for developing theories of fluid flow and fluid flow parameters, such as transport properties, gas kineticists find they have to turn to engineering methods to analyze their data.

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