

The gas property most affected by internal degrees of freedom is thermal conductivity, since energy may be transported in the forms of both translational and internal energy. Inelastic collisions may be treated as small perturbations, and a linearized theory that contains the relaxation time as a parameter may be obtained. This theory accounts for most of the anomalous behavior of polyatomic molecules. In the case of polar molecules, resonant collisions become important since they are most effective in stopping the diffusion of internal energy.

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Relaxation Phenomena *in the* Kinetic Theory of Gases

In general, there are two ways of correlating the properties of gases. One approach is essentially empirical curve fitting, in which an arbitrary equation with several adjustable parameters is fitted to the experimental data. This method has the disadvantage that an extrapolation into an uninvestigated regime may go awry; as the temperature range over which experimental data are available has widened, this has proved to be the case rather frequently. Thus, the second approach—basing all correlations on fundamental principles—has become more desirable, practically, and it has always been more satisfying from a scientific point of view.

In its first stages, the kinetic theory of gases was accepted by most scientists as a good working hypothesis and by others with a great deal of doubt. Today, it is regarded as being almost as firmly based as the first and second laws of thermodynamics. The calculation of transport properties—the coefficients of shear viscosity, diffusion, thermal diffusion, and thermal conductivity—was first successfully carried through by Maxwell for molecules repelling one another as the inverse fifth power of the intermolecular separation. All subsequent investigations in the next fifty years, mainly by Meyer, Stefan, and Boltzmann, were based on the mean-free-path theory, a rather crude approxi-

mation, which agreed only qualitatively with experiment. After 1910, this approximation was superseded by the efforts of Chapman and Enskog, working independently, who succeeded in expressing the transport coefficients in terms of integrals over all possible trajectories traversed by two colliding molecules—the so-called collision integrals. Their theory is valid only for structureless, spherically-symmetric molecules, that is, molecules that have no internal degrees of freedom (e.g., rotational, vibrational, and electronic energy levels, and that interact with a force that depends only on the distance of separation between the centers of mass. These conditions are satisfied, to a high degree, by the rare gases; accordingly, these are the substances for which the kinetic theory has achieved its greatest success. It is possible to measure a transport property of a rare gas over a range of temperatures and to fit the resulting data with a set of collision integrals calculated from a single intermolecular force law with several adjustable parameters. This potential, its parameters now fixed by the previous experiment, proves sufficient to describe the transport coefficients as well as such other properties as second virial coefficients, scattering of molecular beams, and the intermolecular distance and vibrational force constant in the crystal at 0°K.

Thermal Conductivity of Polyatomic Molecules

The same procedure has proved successful, in most cases, for nonpolar, or very slightly polar, polyatomic molecules. This is so even though *none* of these satisfies strictly the original restrictions on the Chapman-Enskog theory. For instance, oxygen has rotational degrees of freedom which are excited at ordinary temperatures. Also, the potential will depend on the angles describing the relative orientation of the two molecules as well as on the intermolecular distance, since oxygen molecules are not spherically symmetric. Since the Chapman-Enskog theory is successful even for molecules like oxygen, it is apparent that the effect of the angular dependence of the potential is slight, or may even be ignored, when considering the viscosity and the diffusion coefficients. However, the coefficient of thermal conductivity is another story; while the discrepancies between experiment and the unmodified elementary theory are very large, the reason for the discrepancy is clear.

If in Fig. 1 we consider a gas with a temperature gradient, i.e., $T_A > T_B$, molecules are continually drifting from one region to the other, carrying with them, on the average, their translational kinetic energy $3kT/2$. When molecules from different regions collide, they will be deflected from their original line of travel; the net effect is a reduction in the rate of transport of energy across the plane indicated by the broken line. Although energy is transferred in a collision from a more energetic molecule to a less energetic one, the transfer is never complete, and so our statement still holds. If the particles have internal degrees of freedom, the internal energy may also be transported by a diffusion mechanism. If inelastic collisions

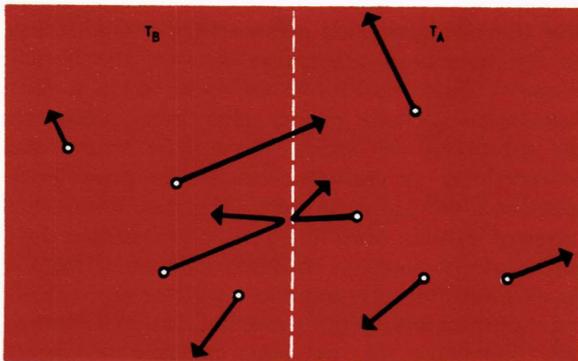


Fig. 1—Possible paths traversed by molecules (represented by circles) in a gas where a temperature gradient $T_A > T_B$ exists. Note that normal drift allows molecules to transport energy across the imaginary boundary (indicated by the broken line) and that collisions impede this flow.

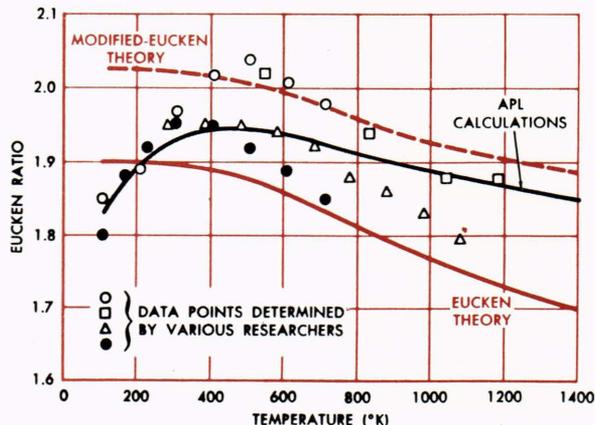


Fig. 2—A plot of the Eucken ratio $f = \lambda M / \eta C_v$ for N_2 as a function of temperature.

sions (collisions resulting in a change in the internal state) are assumed to be relatively improbable, yet frequent enough to maintain the distribution of internal quantum levels close to a local equilibrium distribution, a simple mean-free-path theory calculation yields a relation between the density ρ , thermal conductivity λ , viscosity η , molecular weight M , and the constant volume heat capacity C_v . The latter may be divided into two parts, C_v^{tr} and C_v^{int} , the constant volume heat capacities for the kinetic energy of the center of mass (or translational energy) and for the internal degrees of freedom, respectively. This was first carried out by Eucken who wrote, essentially intuitively,

$$\frac{\lambda M}{\eta} = f_{tr} C_v^{tr} + f_{int} C_v^{int}, \quad (1)$$

where f_{tr} and f_{int} are numerical constants. For structureless molecules, the Chapman-Enskog theory gives $f_{tr} = 5/2$, and Eucken assumed that this same value holds for polyatomic molecules. A simplified mean-free-path calculation then yields $f_{int} = 1$.

A more sophisticated argument initiated by Ubbelohde and developed by Meixner, Chapman and Cowling, and Hirschfelder, notes that each internal quantum state may be regarded as a different molecular species, and assumes that the internal energy is transported by diffusion of these molecular "species." This argument leads to

$$f_{int} = \frac{\rho D}{\eta} \quad (2)$$

where D is the diffusion coefficient. This gives a value of f_{int} close to 1.3 for most gases. We term the second approximation the modified-Eucken formula. Unfortunately, as seen, for example, in the experimental data for N_2 in Fig. 2, there are small but unmistakable deviations from both the Eucken and modified-Eucken formulas.

Effect of Inelastic Collisions

About 12 years ago the Chapman-Enskog scheme was extended by Wang Chang and Uhlenbeck to a Boltzmann equation where a quantum-mechanical scattering cross section was substituted for the classical cross section. When we first considered this problem, no application of their theory had been made because of the complexity of the formulas. However, it quickly became apparent that in the limit of infrequent elastic collisions, the modified-Eucken relationship was obtained.¹ One of the results of the Wang Chang-Uhlenbeck theory was the appearance of a volume or dilatation viscosity and a closely related quantity, τ , the relaxation time characterizing the rate at which energy interchanges between internal and translational degrees of freedom. When the average change of internal energy per collision is small relative to kT , the ratio $\eta/p\tau$ (where p is pressure) is also small. The Wang Chang-Uhlenbeck formulas may now be developed in a Taylor series in $(\eta/p\tau)$ with only the first two terms kept. One now finds

$$f_{tr} = \frac{5}{2} \left[1 - \frac{5}{6} \left(1 - \frac{2}{5} \frac{\rho D}{\eta} \right) \frac{C_v^{int}}{R} \frac{\eta}{p\tau} \right], \quad (3)$$

and

$$f_{int} = \frac{\rho D}{\eta} \left[1 + \frac{5}{6} \left(1 - \frac{2}{5} \frac{\rho D}{\eta} \right) \frac{C_v^{tr}}{R} \frac{\eta}{p\tau} \right]. \quad (4)$$

It turns out that only the rotational degrees of freedom appreciably affect τ . It is just as difficult to evaluate τ theoretically as to use the original Wang Chang-Uhlenbeck formulas, but τ can be measured experimentally. It is thus possible to let experiment rather than a computer evaluate the really difficult expression in the theory. Unfortunately, τ has been measured for only a few gases and only around room temperature, but some useful results can still be obtained. An approximate classical formula giving the temperature dependence of τ has been derived by J. G. Parker of this Laboratory. By fitting it to the measured room temperature value of τ for N_2 , the solid line in Fig. 2 was calculated. The agreement with experiment is significantly better, particularly around room temperature, where τ is known with more certainty. From Eqs. (3) and (4) it is seen that relaxation affects the translational and internal energy fluxes in opposite ways. For N_2 at 300°K, for example, f_{tr} and f_{int} take the values 2.16 and 1.58 instead of the 2.50 and 1.3 predicted by the modified-Eucken theory. By remarkable intuition, this had been predicted qualitatively 20 years ago

¹ E. A. Mason and L. Monchick, "Heat Conductivity of Polyatomic Gases," *J. Chem. Phys.*, **36**, Mar. 1962, 1622-1639.

by Schaefer, Rating, and Eucken. They noted that the average velocity of transport of translational energy was several times greater than the molecular diffusion velocity (i.e., $f_{tr} > f_{int}$). When the possibility of energy exchange exists, a molecule will transport heat sometimes in the form of translational energy and sometimes in the form of internal energy. The net effect will be an increase in the rate of transport of internal energy and a decrease in the rate of transport of translational energy.

Because f_{tr} and f_{int} are affected in opposite ways, the effects of relaxation partially cancel in their total effect on thermal conductivity. A rather more sensitive and completely independent test of our theory has recently become available. Professor Ludwig Waldmann of Mainz has shown that small dust particles suspended in a gas with a temperature gradient experience a force that depends, among other things, on the translational part of the heat conductivity,

$$\lambda_{tr} = f_{tr}(\eta/M) C_v^{tr}. \quad (5)$$

A measurement made recently by Schmitt, on dusty nitrogen at 299°K, yields $f_{tr} = 2.17$, which agrees well with our theory.

Resonant Collisions

In general, there are almost no data on rotational times in polar gases. One may still use Eqs. (3) and (4) and treat τ as an empirical quantity. When this is done for strongly polar substances, physically unrealistic values are often obtained. A closer look at the theory reveals that a particular type of collision has been omitted: *resonant* collisions in which two molecules may interchange their quantum states. Let us designate the sets of rotational quantum numbers of two molecules a and b by $\{\eta_a\}$ and $\{\eta_b\}$. Then, at the start of a collision when the interaction of the two is still negligible, the wave function for the internal variables is separable into a product of the internal wave functions of the two:

$$\psi_i = \psi_a(\{\eta_a\}) \psi_b(\{\eta_b\}).$$

During the course of a collision where a finite interaction matrix element exists between the two states, the perturbation splits the initial state into two "resonant" states

$$\psi^\pm = \frac{1}{\sqrt{2}} [\psi_a(\{\eta_a\})\psi_b(\{\eta_b\}) \pm \psi_a(\{\eta_b\})\psi_b(\{\eta_a\})].$$

The probability of finding the system in the state $\psi_a(\{\eta_b\})\psi_b(\{\eta_a\})$, where an exchange of quantum states has occurred, will be a function of the distance of closest approach. As R varies from 0 to

some critical value R_c , it will oscillate wildly between 0 and 1. Thereafter it will decrease uniformly to zero.

For grazing, *nonresonant* collisions generally, the molecules are deflected only slightly from their original paths; this is shown as the full lines in Fig. 3. The transport of heat is not appreciably affected by these collisions. In a grazing, *resonant* collision, however, the net effect is as if the molecules had been deflected through 180° ; they act so as to decrease the flux of internal energy. It turns out that for polar molecules the number of resonant collisions with finite first-order interactions is much less than the number of nonresonant collisions. This is probably true of nonpolar molecules as well. However, due to the very long range of the dipole-dipole interaction, the energy-exchange cross section for polar molecules is compensatingly large, and this may result in an appreciable decrease in the rate of flow of internal energy. The net effect is to replace the diffusion coefficient D in Eqs. (3) and (4) by $D/(1 + \Delta)$, where Δ can be calculated from the theory of resonant collisions. In Table I we have tabulated values of Δ for H_2O and HCl , together with observed values of the so-called Eucken ratio, $f = \lambda M / C_v \eta$, and values of f calculated by the Eucken and the modified-Eucken theories. Note that the observed values of f are appreciably smaller than either of the calculated values. This is caused by the large value of Δ , which greatly reduces the value of f_{int} . No experimental values of τ for H_2O and HCl are known, so we cannot make a direct test of our theory, but if we treat τ as a disposable constant, our theory can be fitted exactly to the observations. The necessary value of τ is given in the last column of the table in the form of the collision number Z , the average number of collisions required to exchange rotational and translational energy. These values of Z are very reasonable.

In summary, this theory appears to account satisfactorily for practically all the known anomalies

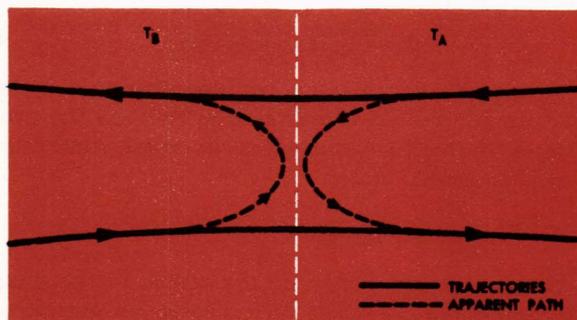


Fig. 3—Real and apparent trajectories for a resonant grazing collision.

TABLE I
OBSERVED AND CALCULATED DATA FOR
TWO POLAR GASES

Substance	Temperature (°K)	Correction (Δ)	Observed Value of $f = \frac{\lambda M}{C_v \eta}$	Values of f According to		Collision Number (Z)
				Eucken Theory	Modified-Eucken Theory	
HCl	294	0.490	1.69	1.90	2.03	3.0
	326	0.419	1.70	1.90	2.03	3.0
	371	0.344	1.69	1.90	2.03	3.0
	424	0.279	1.70	1.90	2.03	3.0
	475	0.232	1.71	1.90	2.02	3.0
	524	0.196	1.72	1.89	2.02	3.0
H_2O	373	0.876	1.32	1.73	1.89	4.0
	393	0.804	1.34	1.72	1.89	4.0
	413	0.741	1.36	1.72	1.88	4.0

in the heat conductivity of gases. If the theory can be further verified, one would have confidence in using it to calculate rotational relaxation times from heat conductivity measurements—a far easier procedure than present methods of measuring such relaxation times.

Application to Other Transport Properties

The same linearization method that was applied to the thermal conductivity may also be applied to the other transport properties. An approximate argument shows that the viscosity and diffusion coefficients are insensitive to relaxation effects. Moreover, since for most temperatures the average energy exchanged per collision is much less than the average kinetic energy, inelastic collisions have only a negligible effect on the trajectory. A quantum effect still remains in the simplified formulas because one must sum not only over all possible collisions for each pair of colliding molecules, but over each possible pair of quantum states as well. In other words, there are infinite potential energy curves that a pair of molecules may follow. The success of a single empirical potential for nonpolar molecules indicates that the effect of nonsphericity for these molecules on transport properties is slight, as was remarked previously. For strongly polar molecules we have found that this is not true. We have replaced the sum-over-rotational quantum states by an analogous classical model.^{2,3}

² L. Monchick and E. A. Mason, "Transport Properties of Polar Gases," *J. Chem. Phys.*, **35**, Nov. 1961, 1676-1697.

³ E. A. Mason and L. Monchick, "Transport Properties of Polar Gas Mixtures," *J. Chem. Phys.*, **36**, May 1962, 2746-2757.

Empirically, it is known that most of the deflection in a collision takes place at the distance of closest approach. A short calculation shows that the average time required for a molecule to rotate 360° is comparable to the time required to complete a head-on collision. We therefore assume that in a given collision, only one relative orientation of the dipoles is effective, and we evaluate the collision integral as if the orientation were fixed at one value throughout the collision. Different collisions correspond to different fixed orientations, but in any one collision the potential is now effectively spherically symmetric. This assumption shifts the emphasis of the problem from the extremely difficult collision dynamics of rotating dipoles back to the kinetic theory and makes the problem a solvable one. We have evaluated the necessary collision integrals for the Stockmayer (12-6-3) potential usually used for polar gases, and compared the results with experiment. The overall agreement is

comparable to that obtained for nonpolar gases with the Lennard-Jones (12-6) potential.²

Although practically no measurements have been made on mixtures of two polar gases, many measurements are available on mixtures of a polar and a nonpolar gas. Our classical model can be easily extended to mixtures using rather simple combining rules, with results for diffusion coefficients and viscosities which are generally of the order of experimental scatter (5 to 10% for diffusion and 1 to 2% for viscosity). Thermal diffusion results are potentially the most interesting since they are very sensitive to the intermolecular forces; but experimental data are scanty. The results, however, look promising.³

In short, the transport properties of polar gases and polar gas mixtures can now be calculated with about the same degree of confidence as has been possible for some years for nonpolar gases and their mixtures.

ADDRESSES

The listing below comprises the principal recent addresses made by APL staff members to groups and organizations outside the Laboratory.

- W. Liben, "Present Status of Micro-electronic Circuitry," *Institute of Radio Engineers*, Washington, D. C. Section, May 17, 1962.
- W. A. Good, "Testing of HT-3," *Society of Automotive Engineers*, A-18 Committee Meeting, Minneapolis, May 18, 1962.
- W. H. Avery, "Possibilities of Hypersonic Flight," *National Research Centre*, Cairo, Egypt, May 18, 1962.
- W. H. Avery, "Engineering Aspects of Hypersonic Flight," *Institute of Engineers*, Cairo, Egypt, May 19, 1962.
- W. H. Avery, "Transit System," *National Research Centre*, Cairo, Egypt, May 21, 1962.
- F. E. Nathanson, "Coherent Search and Acquisition System," *Eighth Annual Radar Symposium*, University of Michigan, June 6, 1962.
- R. W. Cole, "Transit Reliability," *Seventh Military-Industry Missile and Space Reliability Symposium*, San Diego, June 18-21, 1962.
- R. E. Davis, "Radioisotope Power System Operation in the Transit Satellite," *American Institute of Electrical Engineers*, Aerospace Transportation Conference, Denver, June 17-22, 1962.
- M. L. Hill, J. M. Akridge, and W. H. Avery, "Thermal Insulation for Hypersonic Vehicles," *American Society of Mechanical Engineers*, University of Maryland, June 26, 1962.
- T. Wyatt, "The Transit Navigational System," *American Society of Mechanical Engineers*, University of Maryland, June 26, 1962.
- W. Liben, "Microelectronics," *Research Society of America*, Ft. Belvoir, Va., June 27, 1962.
- J. O. Artman and J. C. Murphy, "Hemihedral Field Effects in the Spectrum of Ruby," *First Inter-*

- national Conference on Paramagnetic Resonance*, Hebrew University of Jerusalem, Israel, July 16-20, 1962.
- D. W. Fox, "Estimation of Eigenvalues Based on Operation Comparisons," *International Symposium on Local Properties of Perfect Crystals*, Batelle Institute, Carouge-Genève, Switzerland, July 16-24, 1962.
- I. Katz, "Radar Reflectivity of the Ocean Surface for Circular Polarization," *International Scientific Radio Union*, *Institute of Radio Engineers*, Washington, D. C., May 3, 1962.
- H. W. McLaughlin, "Bi-Static Reflectivity from the Ocean Surface," *International Scientific Radio Union*, *Institute of Radio Engineers*, Washington, D. C., May 3, 1962.

JOURNAL PUBLICATIONS

The following list is a compilation of recently published books and technical articles written by APL staff members.

- M. L. Hill, E. W. Johnson, R. Itoh, and R. L. Readal, "Determination of Composition and Pressures over the Melt in a Vacuum Arc Furnace," *Transactions of the Eighth National Vacuum Symposium*, Vol. II, Pergamon Press, 1961, 749-756.
- M. L. Hill, "Automatic Apparatus for Measuring Gas Evolution Rates," *Transactions of the Eighth National Vacuum Symposium*, Vol. II, Pergamon Press, 1961, 813-816.
- E. P. Gray and D. E. Kerr (JHU), "The Diffusion Equation with a Quadratic Loss Term Applied to Electron-Ion Volume Recombination in a Plasma," *Annals of Physics*, 17, Feb. 1962, 276-300.
- S. N. Foner and R. L. Hudson, "Ionization and Dissociation of Hydrogen Peroxide by Electron Impact," *J. Chem. Phys.*, 36, May 15, 1962, 2676-2680.
- S. N. Foner and R. L. Hudson, "Mass