

THEORIES OF LIQUID VISCOSITY¹

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I. INTRODUCTION

The purpose of this review is to enable the reader to learn the present status of attempts to construct theories of the viscosity of liquids. As a great deal already has been written on this subject, it will not be necessary in most cases to provide a detailed discussion of individual theories. Attention will be given instead to the basic principles involved in some of the theories currently of interest, such as the fluctuation-dissipation theory, and quantum hydrodynamics. An elementary exposition of the mathematical techniques used in these theories is included. The reasons why previous theories of liquid viscosity are unsatisfactory also will be discussed. Topics such as linear and non-linear hydrodynamics, bulk viscosity, rheology and turbulence are briefly surveyed. References are given to review articles and books covering macroscopic and micro-

scopic theories in more detail (see also the "Guide to the Literature" at the end).

A. THEORY OF GAS VISCOSITY²

The classical kinetic theory of gas viscosity furnishes a good example of the type of theory one would like to have for liquids. Starting from the assumption that a gas is composed of elastic spheres whose diameter, while finite, is small compared to their average distance of separation, Maxwell deduced by an argument of admirable simplicity and generality the result that the viscosity of a gas should be independent of density and proportional to the square root of the absolute temperature. Later he showed that if the atoms instead repel each other with a force inversely as the fifth power of their distance of separation, the viscosity is still independent of density but proportional to the temperature itself. These consequences of the kinetic theory were published before any extensive measurements of gas viscosity were available; indeed, Maxwell had to measure the viscosity of air himself in order to test his theory. The confirmation of theory by sub-

¹ Work done under auspices of the U. S. Atomic Energy Commission.

² For references and further details on the development of the kinetic theory of gas viscosity, see ref. (80). For Glossary of Symbols, see p. 537.

sequent experiment thus helped to establish the theory, particularly since the alternative static theory of gases, and common experience with liquids, could not have suggested such behavior.

Maxwell's theory was based on the idea of a mean free path introduced earlier by Clausius. If different "layers" of a gas are moving at different average speeds (*i.e.*, there is an externally imposed velocity gradient), atoms from a "fast" layer can wander over to a "slow" layer, and by colliding with atoms in it they will transfer some of their excess velocity to them. Assuming a constant velocity gradient, one sees that the average difference in velocity between the layer from which the atom came and the layer in which it collides with another atom will be proportional to the distance it has traveled. The rate at which such transfers take place is proportional to the density and to the average velocity throughout the gas. Equating the viscosity coefficient to the rate of change of momentum for unit velocity gradient, one gets by this argument the formula

$$\eta = k\rho\bar{v}\lambda \quad (1)$$

where $\rho = Nm$ is the density, \bar{v} the mean velocity, λ the mean free path and k a numerical constant. The mean free path is inversely proportional to the collision frequency, which in turn is simply proportional to the total cross-sectional area of all the atoms in a layer

$$\lambda = k'/N\sigma^2 \quad (2)$$

and hence the viscosity coefficient is

$$\eta = kk'm\bar{v}/\sigma^2 \quad (3)$$

The viscosity is thus independent of density and proportional to the square root of the absolute temperature, as mentioned above; the constant kk' is of order of magnitude unity. (Its precise determination occupied the attention of Maxwell's successors for some time.)

In Maxwell's second, more general, theory, the viscosity coefficient was expressed in terms of the interatomic force law and the velocity distribution function. The latter was known only for systems in equilibrium, but for one special case, the inverse fifth power repulsive force, it dropped out of the expression, and Maxwell was able to show that the viscosity is then proportional to the absolute temperature. Later, Lord Rayleigh showed by dimensional arguments that for atoms repelling with an n th power force the viscosity must vary as the $((n+3)/(2n-2))$ power of the temperature. Chapman and Enskog both obtained the complete solution to the problem by finding the nonequilibrium velocity distribution function; Enskog did this by solving Boltzmann's integrodifferential equation, Chapman by an equivalent though superficially different method. It is particularly important to note that the numerical constants eventually were calculated fairly precisely, so that the viscosity of a gas could be re-

lated directly to the properties of the atoms composing it; and, in 1924, Lennard-Jones thus was able to deduce the force law for various atoms from measurements of gas viscosity (302). (At present there is little hope of doing this from liquid viscosity data despite four decades of subsequent theoretical research.)

B. DIFFERENCE BETWEEN THE MECHANISMS OF LIQUID AND GASEOUS VISCOSITY

Following the complete acceptance of Maxwell's theory of gas viscosity, and its later refinements by Chapman and Enskog, it has become customary since Graetz (187) to begin theoretical discussions of liquid viscosity by pointing out that the mechanism of momentum transport must be different from that in a gas. Instead of transporting momentum by their own motion from one layer to another, the atoms, it is asserted, transfer it to their neighbors by the action of interatomic forces. The density of a liquid is usually so high that the average distance between atoms is not much greater than the range of these forces.

This seems to be a perfectly reasonable explanation; in fact, 150 years ago anyone who believed in atoms would probably have given exactly the same explanation. It is only because of the counterexample of gas viscosity that we tolerate continual repetition of this old "common-sense" explanation of liquid viscosity.

However, the statement that viscosity is due to interatomic forces by no means constitutes a scientific theory. It is necessary to show that the assumption of some specific type of force law, not too different from the laws assumed in other successful theories, leads to correct predictions of the value of the viscosity coefficient over the entire range of temperatures and pressures. We are certainly nowhere near having achieved this, at least if one judges by the standards applicable to gas theory. Instead, we have a large number of competing "theories of viscosity," ranging from those which do no more than suggest explanations for the factors introduced into empirical formulas, to those which subject the unfortunate reader to hundreds of complex mathematical equations without rewarding him with any real solution to the problem. As yet, there is no general agreement on whether viscosity is essentially due to attractive or repulsive forces; furthermore, although one of the most popular theories uses quantum-mechanical concepts such as tunneling through potential barriers and virtual intermediate states, it has not been proved that the introduction of quantum mechanics is really necessary in order to explain viscosity at ordinary temperatures.

The major criticism applicable to most of these theories is that they merely attempt to explain facts already known, without trying to predict new ones. There is no longer much possibility of *predicting* any new features of the Newtonian viscosity behavior of

simple liquids, since most of them already have been investigated experimentally over the entire liquid range of temperatures; the prediction of Batschinsky's theory, that viscosity is independent of temperature at constant volume, was falsified by Bridgman's measurements at high pressures (69). Deprived of other opportunities of confirmation by successful prediction, theories of viscosity must instead be judged on other grounds. They should, for example, be able to deduce correct formulas for viscosity without employing any assumptions not already verified by experiments on equilibrium properties. Furthermore, one is entitled to expect higher standards of mathematical rigor, since it is well known that it is not difficult to choose the right approximations if one already knows the answer one wants to get.

There are of course some exceptions, notably the recent investigations of Kirkwood (273, 551) and some earlier papers of Andrade (13), in which it was attempted to deduce the absolute numerical value of the viscosity of particular liquids at particular temperatures without employing any molecular constants not already known. These theories apparently were abandoned by their authors, not because they did not lead to sufficiently accurate results, but because they could not be generalized without introducing adjustable parameters.

C. THEORIES AND EXPLANATIONS

In trying to gain an over-all view of the subject of liquid viscosity, one soon realizes that scientists from several different disciplines are concerned with it, and a theory considered satisfactory by one group is often quite unacceptable to the others. To describe this situation it is helpful to classify theories and theorists into four groups, according to whether the emphasis is placed on microscopic or macroscopic description, and whether the attitude toward theory is "pragmatic" or "fundamentalist." (The meaning of these words in this context soon will be made clear.)

Chemists and physicists are generally more interested in microscopic theories, and one might say that chemists tend to be more pragmatic and physicists tend to be more fundamentalist. It is conceded at the outset, however, that there are so many exceptions that these occupational labels should not be taken very seriously. We have in mind the chemist who is primarily concerned with measuring the viscous properties of various compounds and mixtures, and with correlating viscosity with other physical properties and with chemical constitution. For the "pragmatic" chemist, a theory is a relation between two or more measurable properties, which may involve a few adjustable constants, and its success is determined by finding whether the experimental points lie nearly on the theoretical curve. If a theory fails to pass this test, it does not necessarily have to be rejected; it may be "improved" by including

other factors, or by choosing a more complicated relation with more adjustable constants (245, 328). It is desirable to be able to explain the theoretical relation on a molecular basis, and to show that the improved formula takes account of some physical or chemical effect, but such explanations usually must be proposed on an intuitive basis because of the complexity of the molecular processes actually involved.

The "fundamentalist" physicist, on the other hand, believes that a theory is a logical deduction of the consequences of one or more hypotheses. It should predict a definite result which can be proved or disproved by experiment. A successful theory is not one whose consequences agree with experiment—since one never can be sure that a theory based on completely different hypotheses would not also agree with experiment—but rather one which predicts results so unmistakably in conflict with experiment that there is no doubt as to the falsity of the hypotheses. A theory is not acceptable unless it is possible to disprove it (405, 535). In this way the number of hypotheses consistent with (even though not proved by) experiment is gradually reduced. This might seem a negative sort of progress, but to many physicists it is the only real progress which can ever be expected. Of course in the process a number of hypotheses survive so often that they come to be generally accepted as true, and it is only when a "well-established" hypothesis (*e.g.*, conservation of mass or of parity) is disproved that we are forced to realize the provisional nature of the others.

Both chemists and physicists accept the kinetic theory of gas viscosity, because it manages to satisfy the requirements of both. The problem of liquid viscosity, on the other hand, provides a choice example of the difference in attitude of the two groups. The physicist is reluctant to tackle any problem unless there is a chance of getting a definite solution to it, and up to now this has meant that only liquids composed of atoms with spherically symmetric forces, preferably of very short range, could be considered. The largest amount of effort has been devoted to the hard-sphere model, despite the fact that such a model cannot possibly simulate the temperature-dependence of the viscosity of liquids. (Its viscosity is proportional to $T^{1/2}$ at all densities.) The chemist realizes that it is impractical to expect an exact mathematical treatment for the liquids in which he is really interested, yet he would like to be able to make some use of his knowledge of molecular structure and not simply juggle empirical formulas. Thus he proposes a "mechanism" for viscous flow, or a reason why viscosity should be related to the heat of fusion or vaporization or the surface tension, and he believes that such a "theory" aids his understanding of nature. This may be the case, yet it seems not unreasonable to demand that these explanations be proposed before, not after, the experiment is done.

Among those concerned only with macroscopic description there are also fundamentalists and pragmatists. The former are often the specialists in fluid dynamics. Most of them have been trained as mathematicians and cannot abide the physicists' and chemists' neglect of mathematical rigor, yet they are professionally concerned with some very practical problems. To the fluid dynamicist, the viscosity coefficient is just a constant multiplying some rather inconvenient terms in an equation he has to solve, and he is more interested in finding a way to eliminate those terms than in trying to explain why the constant has a particular value. He prefers to treat fluids as continuous bodies described by certain differential equations, even though he knows they are made of atoms and molecules (508). He regards the kinetic theory of gases as suspect on mathematical grounds (it depends on an infinite series which has not been proved to converge) and incapable of describing the properties of real fluids as accurately as he needs to know them.

Finally we come to the engineer or practical rheologist, who actually does need to know how a particular substance behaves under large deformations. Not only does he require the viscosity of simple fluids at various temperatures, but he also must deal with many substances whose flow properties cannot be described by a single viscosity coefficient but rather depend on the amount of deformation or on the previous history as well. The rheologists can be further classified according to their attitudes toward theoretical models (189, 462), but enough has been said to indicate the wide divergence of opinion which is encountered.

It is interesting to compare the present situation in the theory of liquids with that in atomic theory in the last part of the nineteenth century. Before Bohr's quantum theory, physicists proposed a number of models to represent atoms; while the simple billiard-ball model was most often used for kinetic-theory calculations, it was generally realized that something more complex would be required to account for the properties revealed by the spectroscope. Attractive or repulsive forces varying as some inverse power of the distance occasionally were proposed, but the lingering distrust of "action at a distance" caused such arbitrary hypotheses to be regarded as no more than temporary expedients. More popular were models like the "vortex" atom championed by Lord Kelvin and others; it was hoped that atoms, and thus all matter, could be reduced to local disturbances in a continuous medium filling all space. The mathematical treatment of the interaction of as few as two vortices turned out to be so difficult that no one really knew whether the model could legitimately be used to explain atomic properties; on the other hand, anyone could propose a qualitative vortex-atom explanation of some phenomenon without much risk that calculations would prove him wrong.

The result was a "theory" which could explain anything, if one's imagination was good enough, yet could not be disproved, because no one could rigorously deduce its consequences.

The tendency to "explain" the macroscopic properties of matter by attributing hypothetical properties to atoms was criticized by a group of positivists or "energeticists" of which one of the leaders was the chemist Wilhelm Ostwald. The positivists claimed that the purpose of theory is not to explain but to describe and predict; hypotheses about atoms and ether, which cannot be directly observed, are useful only if they enable one to arrive at a satisfactory theory which can be used to predict the results of future experiments as well as to provide a systematic classification of known facts. It was claimed that these hypotheses were being taken too seriously, the result being that physicists wasted their time in speculation and controversy about the "real nature" of atoms and molecules—a subject which was properly part of metaphysics, not physics.

It is interesting to note that chemists, contrasted with physicists, did not indulge these speculations in the nineteenth century. While Dalton's atomic theory was accepted as a convenient basis for the description of chemical reactions, anyone who dared to discuss the actual geometrical arrangements of atoms in a molecule was likely to be subjected to severe ridicule. This conservative attitude left the chemists unprepared for the revolution in physics in the first part of the twentieth century—a revolution which established the reality of atoms while at the same time stripping them of most of the properties with which they had previously been endowed. The atomists like Boltzmann, against whom the positivists had directed their attacks, apparently were vindicated by this revolution; their speculations and calculations had eventually led to a successful atomic theory. But once the new theory, quantum mechanics, had been established in its present form, many physicists gave it a positivist interpretation and declared that any property of an atom which could not be measured was not a real property, and hence was meaningless to discuss. The chemists then borrowed from theoretical physics the rich vocabulary of quantum mechanics, but failed to absorb its positivist viewpoint toward physical theory—a viewpoint which many of their own predecessors had held. Chemists have tried to use quantum-mechanical concepts to explain chemical phenomena, but since it is impossible to do the mathematical calculations exactly for most problems of chemical interest, they have been reduced to qualitative "intuitive" explanations not unlike those which used to be based on the vortex atom.

The influence of both of those historical antagonists, Boltzmann and Ostwald (252), can still be seen in the chemists' concept of liquid viscosity. Ostwald's attempt to reduce all physical phenomena to transformations of

energy is reflected in the present-day popularity of concepts like "energy of viscosity," combined with the statistical view of molecular processes, introduced by Maxwell and made so popular by Boltzmann that practically every theory of viscosity brings in sooner or later the "Boltzmann factor" (141, 397).

Yet one wonders whether such hybrids are really viable. Like a feudal society whose traditional beliefs have been undermined by contact with a more advanced, more materialistic civilization, chemistry has seen its postulational basis subverted by atomic physics. It seems no longer possible to maintain a precise hypothesis about the collective motions of atoms and molecules, for any such hypothesis inevitably is regarded as approximately deducible from the Schrödinger equation. If the hypothesis in its original form turns out to be wrong, one can always find a plausible reason for modifying it. While a theory that can explain all the phenomena is very attractive, in the long run our need to have *only one* explanation imposes a rigorous selection process which weeds out theories whose constants are not constant and whose mathematical deductions are not strict.

In the last section of this article we shall discuss a theory which attempts to describe and predict the viscous properties of a liquid—helium II—by postulating certain collective motions in a manner consistent with quantum mechanics, yet not depending on an exact or approximate solution of the Schrödinger equation for the individual helium atoms. This theory, due to Landau and Khalatnikov (261, 262, 293, 294, 295, 296), provides an extremely interesting case study in scientific method; it may indicate a way out of the difficulties just discussed, though its history also shows the strength of the pressures toward "atomizing" any macroscopic or semi-macroscopic theory. Another example is Jaffé's theory of liquids (251), in which several properties including viscosity are deduced from a minimum number of hypotheses and parameters. Overshadowed by the more ambitious (if ultimately less successful) efforts of Kirkwood (270, 273, 551) and of Born and Green (58), this theory received little notice from physicists; and since it did not cater to current fashion by linking its hypotheses to molecular mechanisms, it was also ignored by chemists.

As this review does not, like some others, accord the place of honor to the rate theory of viscosity, it should be noted to its credit that the rate theory can be applied to non-Newtonian flow without introducing any additional hypotheses (268, 537). Such applications will give a better indication of the validity of this theory than the controversies about whether the energy of viscosity should vary with temperature.

D. EMPIRICAL RELATIONS BETWEEN VISCOSITY AND OTHER PROPERTIES

An empirical formula giving a functional relationship

between viscosity and some other physical property is, in a sense, a legitimate theory, though a rather trivial one. Hypothesis and prediction are identical, even though the importance of the latter often is neglected in practice; it appears that most experimenters take their data and then find the formula which best fits them. This process has provided profitable employment for chemists for the last hundred years, the chief result being a library of formulas, each containing one or more adjustable constants which are tabulated for various liquids. No one formula works for all liquids, nor can one predict accurately the value of the constant which will be needed for a particular liquid. But empirical formulas do at least provide a convenient means for presenting experimental data in a form which is useful to others.

Gambill (172) says that the best formula to use when no experimental data are available is one proposed by Thomas (495)

$$\eta = (0.1167\rho_L^{1/2})10^\alpha \quad (4)$$

where $\alpha = B(T_c - T)/T$, T_c = critical temperature, η = viscosity in centipoises and ρ_L = density in grams/cc. The constant B is made up of contributions from the various atoms and groups in the molecule: *e.g.*, carbon = -0.462, hydrogen = 0.249, double bond = 0.478, etc. The mean error for 108 liquids was found to be 5%, but for 7 other liquids (benzene and alkylene halide) there was a mean error of 39%.

Equation 4 is a special case of a very popular empirical formula

$$\eta = Ae^{E_v/T} = Ae^{E_v/kT} \quad (5)$$

where E_v is the energy of viscosity. Partington (397, see also 119, 418, 481) lists the following formulas, all of which have been proposed and tested for one or more liquids by various experimenters

$\frac{A}{(1 + BT + CT^2)}$	$\frac{C}{A + T} - B$
$\frac{C}{(A + T)^n}$	$\frac{A(T_c - T)}{T - B}$
$\frac{AT^{1/2}[(T - B)^2 + C]}{(D + T)^2 + E}$	$C \left(\frac{T + A}{T + B} \right)^n$
$C A^{\sin \alpha \Delta(T+B)}$	Ce^{-BT}
$A(1 + Be^{-CT})^n$	$CT^{-n}e^{-A/T}$
C/T^3	$\frac{A}{T - B}$
$A - BT - [(BT - A)^2]^{1/2}$	$A^{(T-B)/(T-C)}$
$\frac{(A - BT)^n}{(C + DT)^m}$	$Ae^{B/T} + Ce^{D/T}$
$T(Ae^{B/T} + Ce^{D/T})$	

Some other equations recently proposed are (40, 67, 106, 118, 179, 315, 354)

$$\log \eta = A/T + B \log T - CT - D$$

$$\eta = (A + B/T)^3$$

$$\eta = ATe^{B/T} + CT$$

$$\log \eta = B + AT^{-n}$$

$$\log \eta = -Ae^{D/T}[-Ei(-D/T)] - B + Ce^{D/T}$$

(where $Ei(x)$ is the exponential integral)

$$\log \eta = AT^{-2} + BT^{-1} + C$$

$$\log \eta = A + BT^{-3}$$

A number of other equations involve quantities such as pressure, volume, surface tension, density, velocity of sound, refractive index, vapor concentration, vapor pressure, latent heat of evaporation, latent heat of fusion, molecular weight, and chemical composition.

What seems to be lacking is an accepted set of criteria for testing these empirical formulas. When one is choosing the best value of an adjustable constant, or comparing two formulas with the *same number* of constants, one can simply calculate the mean square deviation of the calculated values from the experimental points, and try to make this as small as possible. But there is nothing to prevent someone else from “improving” the formula by “taking account of” some alleged physical effect—which usually means simply inventing a more elaborate formula with more constants. It is then shown that the new formula fits the data better, and this is taken as a justification of the “theory” which suggested the more elaborate formula (245). Now it is well known that any given set of experimental points can be fitted at least as well, and usually better, by a formula with $n + 1$ constants, as by a formula with only n constants, provided that the former reduces to the latter for some particular value of one of the constants. If one is willing to have as many parameters as one has experimental points, one can obtain a perfect fit, even though the resulting theoretical curve may oscillate wildly in between the points to which it is fitted.

As long ago as 1889, Oliver Lodge wondered “whether chemists are not permitting themselves to be run away with by a smattering of quasi-mathematics and an over-pressing of empirical formulas” (320).

As long as empirical formulas are regarded as just that, there is no reason why they should not be judged by the criteria of accuracy in fitting experimental data and ease of application. It is when the experimenter succumbs to the temptation of “confirming a theory” that he tries to represent his data by one of the monstrous functions listed above. Yet none of the theories of liquid viscosity which proceed rigorously from statistical mechanics is likely to produce a result which can be expressed in terms of a finite number of elementary functions—only approximate theories can do that. While an experimentalist may privately believe that one approximate theory is better than others, it is not up to him to decide the issue in advance by the way in which he reports his data.

II. MACROSCOPIC THEORY

Why does one want to know the viscosity of a liquid? Aside from the insight into the microscopic structure of liquids which may be gained from theoretical interpretations of viscosity measurements, knowledge of viscous flow properties is important in many hydrodynamics problems. This section is an attempt to extract from the vast literature on hydrodynamics a few examples of the way in which the mathematical theories take account of viscosity. The purpose is not to discuss specific technical applications, but rather to see how much of the information which chemists have accumulated about the viscosity of liquids actually can be incorporated into present-day theory.

Only a few feet separate the *Journal of Chemical Physics* and the *Journal of Fluid Mechanics* on the shelf in the library, yet they seem to come from two different worlds. Fluid mechanics is a subject inaccessible to many scientists because it is surrounded by an icy wall of mathematical equations. This is unfortunate, for when one has penetrated the wall one finds much of interest and value. Not the least interesting is the fact that fluid mechanics is the last stronghold of the positivist school of classical physics. While chemists and physicists regard the kinetic-molecular nature of matter as an established fact, the hydrodynamicists still view the kinetic theory with considerable hostility. They are concerned only with macroscopic properties of matter, which they believe can best be described by continuum mechanics, as embodied in a few differential equations. If one equation doesn't work, try another, but the criterion of success is agreement with experiment (and, to a lesser extent, formal elegance), not the possibility of deriving the macroscopic equation from microscopic considerations.

The foremost spokesman for this viewpoint is Clifford Truesdell (508, 510, 513). Unlike some of his colleagues, he is able to criticize the kinetic theory with some authority, having done some work on it himself (242, 512). While Professor Truesdell is willing to concede the existence of atoms, he clearly considers it unfortunate that modern physics and chemistry have to assume the discrete structure of matter; he would like to push continuum mechanics as far as possible before permitting the introduction of the kinetic theory in any problem (505, 510, 514; see also 177, 289).

Synge (489) has shown that the preoccupation with macroscopic variables has resulted in a neglect of useful thermodynamic methods. In particular, some hydrodynamicists are reluctant to use entropy, probably because its physical interpretation is clear only from a microscopic viewpoint. He says: “My guess is that the still prevalent entrophoby (to coin a word) springs from an unwritten law that mechanics should deal only with concepts directly related to ordinary experience . . .

However commendable this common-sense attitude may be, the price we have to pay for it in intellectual confusion is too high . . . Entrophoby must be fought until such time as entropy takes the place it deserves in standard texts on hydrodynamics."

Nevertheless, physical chemists will have to start learning hydrodynamics of a fairly advanced character in the near future. This is because practically everything of value already has been squeezed out of the study of Newtonian shear viscosity; the qualitative viscous properties of simple liquids can be explained equally well by several different crude theories, and hence these properties really give little information. Experiment is now far ahead of rigorous theory, so there seems little need for more detailed quantitative investigations, except for engineering purposes. The most interesting work in the next few years will be that on non-Newtonian flow and bulk viscosity, and here there is bound to be much confusion unless the guidance of hydrodynamic theorists is accepted.

A. VISCOUS FLOW THEORY

Investigations of the flow of viscous fluids are based in principle on three equations expressing the conservation of matter, momentum, and energy, together with the equation of state relating the pressure to the density and temperature. The equation for momentum conservation is usually taken to be that of Navier and Stokes

$$\rho(\partial\mathbf{v}/\partial t) + \rho\mathbf{v}\cdot\nabla\mathbf{v} + \nabla\cdot\mathbf{P} = \mathbf{F}$$

where the pressure tensor \mathbf{P} is assumed to have the form

$$\mathbf{P} = P_0\mathbf{1} - 2\eta(\nabla\mathbf{v})^{sym} - (\nabla\cdot\mathbf{v})\mathbf{1}$$

where P_0 is the equilibrium (hydrostatic) pressure, $\mathbf{1}$ is the unit matrix, \mathbf{v} is the velocity of the fluid at a given point in space, $\nabla\mathbf{v}$ is the velocity-gradient (rate-of-deformation) tensor, and \mathbf{F} is the external force. We continue to use the symbol η for the shear viscosity, though in hydrodynamics μ usually is used. The vector and tensor notation is explained in Section III-B-1.

The Navier-Stokes equation depends on the assumption that there is a linear relation between stress and strain; and it is customary to assume the "Stokes relation" $3\lambda + 2\eta = 0$ in order to eliminate the second viscosity coefficient λ . The first assumption restricts the validity of this equation to Newtonian flow processes, and the second implies that the "bulk" or "volume" viscosity is zero. It would appear that the Navier-Stokes equation is thus inadequate to deal with many phenomena currently of interest, yet Pai says, in the introduction to his recent monograph (392):

From the theoretical point of view, we should, in the main, be content that the fundamental equations of gas dynamics are the Navier-Stokes equations, and that the stress tensor is a linear

isotropic function of the rate of strain tensor with no dissipation of energy in a spherically symmetric expansion or compression, so that there is only one coefficient of viscosity. Even with such simplifying assumptions, it is still not possible at the present time to solve the Navier-Stokes equations for any practical problems because of insurmountable mathematical difficulties. We have to use further assumptions to simplify the Navier-Stokes equations in such a manner that practical problems can be solved. . . .

Present knowledge of the theoretical effects of viscosity is based on a few one-dimensional cases where the Navier-Stokes equation can be solved exactly (184, 288, 392, 510), together with a number of approximate calculations which assume that the effects of viscosity are confined to small regions near fluid-solid surfaces, the flow pattern being that of an inviscid fluid elsewhere (77, 171, 174, 186, 236, 237, 287, 321, 360, 392, 449, 454, 539). This "boundary-layer" theory corrects the theory of inviscid fluids where it is most flagrantly in conflict with experience, *viz.*, in permitting "slip" of the fluid at a solid boundary. The solution of the Navier-Stokes equation changes discontinuously when η becomes zero, since a fluid with very small but finite viscosity cannot slip, while a fluid with zero viscosity can. Complete neglect of viscosity also leads to the prediction that a solid sphere immersed in a stream is not dragged along by it (d'Alembert's paradox).

Viscous effects are often accounted for in shock-wave problems by the use of the von Neumann-Richtmyer approximation (75, 76, 376). Artificial dissipative terms are introduced in the stepwise numerical solution of the equations, in order to give the shock a finite thickness; the extra terms are actually equivalent to a non-linear viscosity, since the viscosity coefficient itself is taken proportional to $|\mathbf{dv}/\mathbf{dx}|$.

In the present century "fluid dynamics" almost always means "gas dynamics"; this becomes clear as soon as one looks at investigations in which the equation of state of the fluid and the variation of viscosity with temperature are specified. The "fluid" turns out to be an ideal gas, whose viscosity is proportional to T^n . It is often alleged that the kinetic theory predicts $n = 1/2$, whereas for "real gases" n is somewhere around 0.8, implying that the kinetic theory must therefore be wrong. (Such statements are usually the result of ignorance rather than malice.) A perusal of recent literature uncovered only a handful of cases in which a variation of viscosity with temperature characteristic of liquids rather than gases was advocated or actually employed, and in none of the calculations did it seem to be very important which mathematical function was chosen to represent this variation (51, 57, 81, 243, 381). One must therefore conclude that it is not lack of knowledge of the precise nature of the temperature-dependence of liquid viscosity which constitutes the major obstacle to progress in fluid dynamics.

B. NON-LINEAR THEORY

There is now a considerable body of literature on non-Newtonian flow, partly because of the engineering or biological importance of many substances with peculiar rheological properties. Attempts to construct a consistent mathematical theory, generalizing the classical linear laws, are described in detail by Truesdell (509); the following paragraphs are based on his earlier simplified presentation (508). Much of the theory is due originally to Reiner (423, 424), whose recent books also should be consulted (422, 425).

Suppose that s is the x, y component of the stress tensor \mathbf{S} , and γ is the same component of the rate-of-deformation tensor \mathbf{G} . (The following remarks also apply to elasticity when \mathbf{G} is the strain tensor; when we specialize to the case of viscosity, \mathbf{G} will be identified with the velocity-gradient tensor $\nabla\mathbf{v}$.) Truesdell begins by pointing out that it is not good enough to "retain the non-linear terms" and write, instead of $s = \eta\gamma$

$$s = \eta\gamma + \eta'\gamma^3 + \dots \quad (6)$$

with the assertion that the linear relation is valid for small rates of deformation ($\gamma \ll 1$). Rate of deformation is not dimensionless and can be given any numerical magnitude whatever simply by an appropriate choice of units. A more serious drawback of eq. 6 is that it is based on the unfounded assumption that shearing stresses alone are sufficient to maintain shearing strains. Actually there is no reason why the x, y component of the matrix \mathbf{S} should depend only on the x, y component of \mathbf{G} . A theory based on this assumption cannot describe the effects discovered by Reynolds and Poynting, who found changes of volume associated with changes of shape. These effects appear even before there are quantitative departures from the linear shearing laws. Poynting's experiments were done with steel wires and rubber cords, and Reynolds' with bags of solid spheres, but similar effects have been observed in liquids. Thus Weissenberg (536), in 1947, found that a liquid between two concentric moving cylinders climbs up the sides of both cylinders and falls in the interspace.

In constructing a general theory, one might start by expanding the stress matrix \mathbf{S} in a power series in the rate-of-deformation matrix \mathbf{G}

$$\mathbf{S} = K_1\mathbf{G} + K_2\mathbf{G}^2 + K_3\mathbf{G}^3 + \dots$$

where K_1, K_2 , etc., are scalars. This turns out to be unnecessarily complicated, since for an isotropic fluid the matrix \mathbf{G} must have certain (tensor) transformation properties, expressing the requirement that physical laws must be invariant under changes of coordinate systems. The invariants of a matrix are its eigenvalues or, more precisely, for a 3×3 matrix, the three symmetric functions of the eigenvalues G_1, G_2 and G_3

$$I = G_1 + G_2 + G_3$$

$$II = G_2G_3 + G_3G_1 + G_1G_2$$

$$III = G_1G_2G_3$$

It can be shown that \mathbf{G}^3 and all the higher powers of \mathbf{G} can be expressed in terms of \mathbf{I}, \mathbf{G} and \mathbf{G}^2 ; for example (Cayley-Hamilton equation)

$$\mathbf{G}^3 = III\mathbf{I} - IIG + IG^2$$

One then obtains the *exact* expression

$$\mathbf{S} = F_0\mathbf{I} + F_1\mathbf{G} + F_2\mathbf{G}^2 \quad (7)$$

where F_0, F_1 and F_2 are power series in the scalar invariants, I, II , and III . Writing out the terms of first, second, and third order, we have

$$\mathbf{S} = (\alpha + AI + BI^2 + CII + DI^3 + E \cdot I \cdot II + F \cdot III)\mathbf{I} + (G + HI + KI^2 + LII)\mathbf{G} + (M + NI)\mathbf{G}^2 \quad (8)$$

The linear terms in Eq. (8) yield the classical laws of viscosity or elasticity; identifying A with the coefficient λ , G with 2η , and α with $-P_0$, one gets the stress tensor of ordinary fluid dynamics

$$\mathbf{S} = -P_0\mathbf{I} + \lambda\mathbf{I} + 2\eta\mathbf{G}$$

In a situation where only shear is present, \mathbf{G} takes the form

$$\mathbf{G} = r \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (9)$$

and we have $I = 0, II = r^2, III = 0$. The stress tensor is then

$$\mathbf{S} = (\alpha + Cr^2) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + r(G + Lr^2) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + r^2M \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (10)$$

In the linear case C, L , and M are negligible; the third-order term, whose coefficient is L , corresponds to the term $\eta'\gamma^3$ in eq. 6. The significant result is that two new effects appear, and they are of order r^2 , whereas the "non linear viscosity" included in eq. 6 is of order r^3 . The first effect, which Truesdell calls the "Kelvin effect" since Lord Kelvin predicted it theoretically in 1883, is an expansion or contraction proportional to the square of the deformation, which results from the term Cr^2 added to the pressure ($\alpha = -P_0$). The second, called the "Poynting effect," is a normal stress in the plane of the motion, arising from the term Mr^2 , which can cause the material to elongate or shorten. The general theory does not, of course, fix the sign of C and M .

The Kelvin and Poynting effects are independent of the classical viscosity effects, the former depending only on even-order terms in r , the latter only on odd-order terms. These conclusions, and the general form of eq. 7, are independent of the choice of units for \mathbf{G} , which affects only the numerical values of the coefficients.

In order to discuss the range of validity of the linear viscosity theory one has to consider not simply the rate of deformation, but some appropriate quantity which does not depend on the choice of units. Since \mathbf{S} has dimensions (mass)(length)⁻¹(time)⁻² while \mathbf{G} has dimensions (time)⁻¹, \mathbf{S} must depend not only on \mathbf{G} but on other quantities such as the thermodynamic state and material constants of the fluid. If the fluid has a characteristic constant t_0 of the dimension of time—this would be true, for example, of any substance which has both a Young's modulus E and a viscosity η , since η/E has the dimension of time—the relation between \mathbf{S} and \mathbf{G} can be put in the dimensionless form

$$\mathbf{S} = (\eta/t_0)g(t_0\mathbf{G}, P_0 t_0/\eta, T/T_0) \quad (11)$$

The thermodynamic variables P_0 and T appear in the function g only in the dimensionless ratios $P_0 t_0/\eta$ and T/T_0 , respectively, where T_0 is some reference temperature such as the boiling point at one atmosphere pressure. If \mathbf{G} is measured by a single magnitude r , as in eq. 9, the criterion of validity for the linear approximation is $rt_0 \ll 1$: "the rate of deformation must be much smaller than the reciprocal time constant of the fluid." A fluid which has a time constant Truesdell calls a "Reiner-Rivlin fluid."

If, on the other hand, the fluid does not have a material constant with the dimension of time, the dimensionless relation between \mathbf{S} and \mathbf{G} would have the form

$$\mathbf{S} = P_0 g(\eta\mathbf{G}/P_0, T/T_0) \quad (12)$$

The "truncation parameter" in the series expansion is now $\eta r/P_0$ instead of rt_0 , and the linear approximation is valid only at low density, low rate of deformation, and high pressure. An interesting consequence of eq. 12 is that the coefficients of viscosity of all orders are independent of pressure. Such a fluid, lacking a time constant, is called "Stokesian" by Truesdell.

C. BULK VISCOSITY

In any general analysis of viscous flow or elastic deformation, at least two material constants must appear, even in a linear approximation. They measure the response of the substance to two different types of forces: those tending to shear it, and those tending to expand or contract it. While the existence of two independent constants seems to be accepted in elasticity theory, most of the standard works on hydrodynamics try to suppress one of these constants by making it simply proportional to the other. A typical rationalization of this policy goes as follows: write out the x, x component of the stress tensor

$$S_{xx} = -P_0 + \lambda I + 2\eta G_{xx}$$

and add to it similar equations for S_{yy} and S_{zz} . The result (recalling that $I = G_1 + G_2 + G_3 = G_{xx} + G_{yy} + G_{zz}$) is

$$S_{xx} + S_{yy} + S_{zz} = -3P_0 + (3\lambda + 2\eta)I \quad (13)$$

It is then argued that the pressure is really the same as the average diagonal element of the stress tensor

$$P_0 = -(1/3)(S_{xx} + S_{yy} + S_{zz}) \quad (14)$$

and hence one must set $(3\lambda + 2\eta)$ equal to zero.

The above definition of the pressure, eq. 14, usually attributed to Maxwell and uncritically accepted by later workers, can be justified only for systems in thermodynamic equilibrium. Its adoption in non-equilibrium situations implies that the pressure always depends only on the temperature and density, through the equation of state, and not on the rate of expansion or contraction of the system (represented by I in eq. 13). The resulting postulate, $3\lambda + 2\eta = 0$, is called the Stokes relation; yet Stokes himself used it only because he realized that in most cases of practical interest the rate of expansion would be so small that the value assigned to the quantity $3\lambda + 2\eta$ would be unimportant (484). Reiner (424) has argued that setting $3\lambda + 2\eta$ equal to infinity, rather than to zero, is equivalent to $I = 0$.

Cohen (90) listed a number of other relations between λ and η proposed by various nineteenth century scientists, and the history of the subject has been reviewed by Truesdell (sec. 61A in ref. 509; also 507, 511). Many theorists treated the two constants as independent and related both of them to molecular properties (88, 138, 349, 507, 535a), but these efforts were generally ignored until about twenty years ago. In 1942, Tisza (497) [cf. 330a, 422, 479, 481a] suggested that λ could be measured in ultrasonic absorption experiments, and since then a number of such experiments have been interpreted by assigning various values to λ . In many cases the Stokes relation is said to be disproved, and large positive values of λ often are reported. Bulk viscosity is also said to be involved in the phenomenon of acoustic streaming (117, 127, 159, 255, 314, 369, 402, 438). References to the original work may be found in the review article by Karim and Rosenhead (256), the book by Herzfeld and Litovitz (222), and the various contributions to the Royal Society discussion (448); see also (10, 19, 22, 36, 44, 45, 62, 76a, 164, 196, 207, 229, 231, 238, 259, 285a, 289, 292, 297, 310, 314-319, 330, 332, 333, 345, 372-374, 400, 401, 403, 422, 425, 435, 437, 471, 475, 476, 532, 547, 551). Nevertheless several recent hydrodynamics textbooks adopt the Stokes relation with little or no discussion (73, 105, 113, 178, 230, 250, 394, 414, 451, 526) or even ignore bulk viscosity completely (47, 48, 68, 78, 145, 208, 303, 466, 485, 543).

Since it is the quantity $3\lambda + 2\eta$ whose existence is in question, we use the term "bulk viscosity" for $\kappa = \lambda + (2/3)\eta$.

While it may be legitimate to ignore bulk viscosity in some physical situations on the grounds that it is multiplied by a rate of expansion which is negligible,

this should be an explicitly stated assumption, like the assumption of incompressibility, and a recognized source of possible error. It is well known in fluid mechanics that the inclusion of ordinary shear viscosity changes the character of the differential equation and the qualitative nature of the flow near a boundary, even though the actual magnitude of the viscosity term is infinitesimal. There may be similar effects when bulk viscosity is included in the differential equation, though the exact mathematical theory has not yet progressed far enough to indicate what actually happens (177, 289, 510). Birkhoff (53) has emphasized the falsity of the belief that "small causes produce small effects"—particularly in hydrodynamics. It would seem that a fluid which expands and contracts indefinitely without dissipation is performing perpetual motion of the second kind and is thus violating the second law of thermodynamics. However, it has been claimed (440) that dilatation produces no irreversible effects in a system of structureless particles.

The existence of a bulk viscosity is usually taken to imply some kind of dissipation or relaxation mechanism on the molecular level. Rapid compression or expansion upsets the equilibrium distribution of energy among translational, vibrational, and rotational degrees of freedom, and if the rate of expansion is greater than the inverse of the "relaxation time" for equilibration, there will be an irreversible absorption of energy. A number of experiments have been interpreted by means of such relaxation mechanisms, sometimes without explicit mention of bulk viscosity (10, 380, 396, 438). It may, of course, turn out that bulk viscosity is strongly frequency-dependent, which would make the linear theory untenable. Instead of considering κ to be a function of I , one should use more terms in eq. 8 [*cf.* Truesdell's remarks, p. 673 of ref. 510]. Unfortunately, the condition that the dissipation of energy be non-negative, which in the linear theory leads to the conditions $\eta \geq 0$, $\kappa \geq 0$, cannot be reduced to any simple conditions on the higher-order coefficients (see sec. 61 of ref. 509; 457).

It also has been suggested that there exists an "intrinsic" bulk viscosity due solely to intermolecular forces, quite apart from any possible relaxation processes; a fluid of hard spheres, with no internal degrees of freedom, would thus have a finite bulk viscosity (138, 371).

In concluding this section, we remark that while it may be possible to imagine an ideal system which has zero bulk viscosity, the burden of proof must certainly be placed on anyone who claims that a real liquid has this rather rare property.

D. RHEOLOGY

The theoretical framework described in Section B is still not general enough for the description of many

real substances, for it is based on the assumption that the stress tensor depends only on the rate-of-deformation tensor. A large number of natural and synthetic products have properties which cannot be described completely either by the theory of viscous fluids or by the theory of elastic solids (in which stress depends only on the *amount* of deformation). The study of the interrelationships of stress, strain, and time is now known as "rheology"; it is a subject long dealt with on an empirical basis, but subjected to systematic mathematical analysis only within the last two or three decades.

Scott Blair's "Survey of General and Applied Rheology" (462) is still an extremely fascinating and useful account of the subject, though it should be supplemented with reviews of more recent work (43, 81, 129, 347, 422, 425, 428, 463, 511, 545). Scott Blair reviews the history of the subject, going back to the early Egyptian water clocks, and distinguishes two schools of rheology, the "analytical" and the "integral." The former school seeks to relate the properties of a material to those of viscous fluids and elastic solids, by considering it to be composed of viscous elements ("dashpots") and elastic elements (springs) whose effects are additive. The latter school avoids the use of models and simply postulates empirical relations between stress, strain, and time. After describing the properties of many interesting substances and methods for measuring them, Scott Blair discusses the various theoretical interpretations in the light of psychophysical experiments. These experiments, which form the basis of the new discipline of "psychorheology," were designed to find out how people perceive such qualities as viscosity and elasticity. While one might suppose that viscosity and elasticity cannot be directly compared because they have different dimensions, it turns out to be possible to establish a psychological equivalence scale, so that one can answer such questions as, "is the viscosity of substance A greater than the shear modulus of substance B?" Accounts of more recent work on psychorheology may be found in Scott Blair's book "Measurements of Mind and Matter" (465) and in articles by Harper (210, 211, 464). Other "cross-modality comparisons" in psychology are described by Stevens (482).

E. TURBULENCE

Whereas rheology is the study of particular *materials* which may never obey the linear laws of viscous flow, the study of turbulence phenomena deals with the *conditions* under which those laws may be invalid for otherwise well-behaved materials, and it attempts to establish other laws valid under such conditions. Presumably any liquid, when forced to move too fast relative to a solid boundary, will abandon the smooth "laminar" flow pattern contemplated by the linear

theory, and its motion will take on a certain random character which cannot be described precisely even by the more general theories we have mentioned.

The condition for transition to turbulent flow is usually given by specifying the value of a dimensionless parameter called the Reynolds number

$$R = vL\rho/\eta$$

where L is a length proportional to the radius of the tube, or to some linear dimension of the solid boundary. In a sense viscosity is responsible for turbulence, since a fluid with vanishing viscosity would have an infinite Reynolds number and would thus perform laminar flow at any velocity. On the other hand, the greater the viscosity, the more rapidly a local condition of turbulence will decay (311). According to Batchelor and Townsend (39), viscous forces are not very important in turbulent motion except in small regions of the fluid near the boundary, or in thin vortex layers.

Theories of turbulence naturally have a strong statistical aspect, but while in many cases they appear to be similar to the kinetic theory of gases, the elements considered are usually small macroscopic regions of the fluid rather than molecules. Yet the physical mechanisms of viscosity and turbulence must be closely related, so that one should be able to develop a theory which accounts for both, at least in gases and ultimately in liquids. ("A truly rational treatment of the problem of turbulent friction is unattainable until the quality of viscosity itself has been rationally analyzed, if this were possible" (145).) There have been some recent attempts along this line but it is too early to judge their success.

III. MICROSCOPIC THEORY

A. CLASSIFICATION OF THEORIES

We begin by listing the various theories, arranged according to the type of physical (rather than mathematical) assumptions which they make. Another property of theories of viscosity, which might have been used as the basis of a classification scheme, is the extent to which the equilibrium properties of a substance (determined either by theory or experiment) determine its transport properties. From the kinetic-theory viewpoint the distinction between equilibrium and non-equilibrium processes is not really fundamental, since both depend on the same molecular motions, and it might be argued that the distinction between classical and quantum-mechanical theories would be more significant. However, it is often useful to adopt a more phenomenological treatment, particularly when kinetic theory results are not available, and it is then of interest to determine the minimum number of material constants on which the observable properties of the substance depend. The only quantum-mechanical theory

which we shall discuss is so completely different from the classical theories that we do not include it in the list at all.

1. Dense Gas of Hard Spheres

By analogy with the theory of equation of state, Gustav Jäger (248) proposed to correct the dilute-gas viscosity formula by taking account of finite molecular size. He obtained an expression of the form

$$\eta = \eta_0(y^{-1} + A + By) \quad (15)$$

where y is a factor correcting the collision rate, which may be determined from the equation of state

$$P_0V/RT = 1 + (4b/V)y$$

and $A = 8b/V$, $B = 16b^2/V^2$; b is the volume occupied by the spheres themselves. The second and third terms become negligible at low density as b/V goes to zero and y goes to 1, and η_0 reduces to the dilute-gas viscosity given by eq. 1. It should be mentioned that y is not an empirical quantity; it can now be calculated theoretically with some accuracy over the entire range of densities (3, 4, 5, 531).

Jäger's theory was generally ignored except by his contemporary Marcel Brillouin, who discussed and extended it in his book (72). Later Enskog (138) derived eq. 15 more rigorously (with $A = 16b/5V$, $B = (0.7614)(16b^2/V^2)$), using a modification of his transport theory based on the Boltzmann equation. Enskog also made more explicit the nature of the changes in the theory needed to take account of the finite molecular size; not only does the collision rate change, but momentum can be transferred "instantaneously" (in a non-relativistic theory) across finite distances when the spheres collide, in addition to the usual momentum transport by motion of molecules from one part of the gas to another.

This type of theory is valid only for hard spheres, since it assumes only two-body collisions. Though it works well up to quite high densities, it is based on an assumption about the sequence of collisions which must eventually break down when the spheres get so close together that each one is trapped in a "cage" and collides only with its nearest neighbors. This introduces a correlation between successive collisions which makes the Boltzmann equation inapplicable, but this effect probably is not important until the system already has condensed to a solid.

Equation 15, insofar as it refers to a system of hard spheres, does not predict any temperature-dependence for the viscosity other than the usual $T^{1/2}$, since changing the temperature merely changes the time scale. However, the third term, which is dominant at high densities, is comparable to some of the empirical formulas which make the viscosity vary inversely as the "free space."

The Enskog theory is reviewed in refs. 88 and 232; and several similar theories have been proposed (66, 71, 100, 103, 122, 182, 233, 326, 327, 430, 434, 472, 480, 520).

2. Monatomic Liquids with Gaslike Structure

In this category we place the theories of Born and Green (58, 59, 194) and Kirkwood (246, 270, 271, 273, 551), and more recent work to be discussed in Section III-B. In a more mathematically oriented classification scheme we would label these "theories based on the superposition approximation for the distribution function, and/or on the theory of random processes." While the distribution function method is general enough to be applicable to any state of aggregation, the approximations usually employed in these theories tend to favor the gaseous rather than the solid concept of liquids. Instead of starting with a completely ordered configuration of molecules and then introducing a small amount of disorder, they start from a disordered state and introduce a short-range correlation in the positions of pairs of molecules.

The superposition approximation, introduced in 1935 by Kirkwood (269), is the assumption that the probability distribution for the simultaneous positions of three molecules can be expressed as a product of the three relevant pair-distribution functions. It has been shown (214, 450) that this assumption leads to correct values for the second and third virial coefficients of a hard-sphere gas, but predicts an incorrect value for the fourth coefficient; and there has been considerable discussion of the propriety of its use in transport theory (82, 158, 181, 276, 377, 410, 523). The basic papers are the following:

Kirkwood and Boggs (272a): The superposition approximation is used to derive an integral equation for the pair distribution function for a fluid of hard spheres; the equation can be solved numerically.

Kirkwood (270): Proposed a general theory of transport processes based on Brownian motion theory. The friction constant in Brownian motion is shown to be related to the autocorrelation function of the force acting on a molecule

$$\zeta = (1/3kT) \int_0^\tau \langle F(t)F(t+s) \rangle ds \quad (16)$$

where $\langle \rangle$ indicates an ensemble average, and τ is the "plateau time" after which the correlation is essentially zero (see also Helfand (217a)).

Kirkwood, Buff, and Green (273): The viscosity coefficient is expressed in terms of ζ (see also ref. 271) and the shear viscosity is calculated for liquid argon at 89°K. It is found that $\eta \sim 2.63 \times 10^6 \zeta$ and a rough estimate of ζ leads to the result $\eta \cong 1.27 \times 10^{-3}$ poise, compared to the experimental value 2.39×10^{-3} poise.

Irving and Kirkwood (246): The equations of hydrodynamics, and the expression for the stress tensor used by Kirkwood, Buff, and Green, are derived from the statistical mechanical theory. Other derivations have been given by Noll (379) and Richardson (440), and the generalization to multicomponent systems was accomplished by Bearman and Kirkwood (41).

Born and Green (58, 59): Proposed a general theory of liquids based on Kirkwood's superposition approximation. The Kirkwood-Boggs integral equation is generalized to molecules interacting with any type of central forces, and the general theory then is applied to transport processes. An expression for viscosity is obtained but not evaluated numerically because of lack of knowledge of the distribution function. It is argued that the expression predicts the correct qualitative variation with temperature for liquids (see also Yang (546) and Higgins and Raw (228)). Green later remarked (195) that it had been assumed that the steady state of a non-uniform fluid depends only on the local values of the macroscopic parameters and their space derivatives: "Unfortunately this assumption alone did not suffice to determine a unique solution of any problem, and to obtain an explicit formula for the coefficient of viscosity, Born and Green had to "guess" the deformation of the molecular structure by the flow."

Zwanzig, Kirkwood, Stripp, and Oppenheim (552): The calculation of the viscosity of liquid argon is revised, using a more accurate distribution function obtained by numerical solution of an integral equation similar (but not identical) to that of Born and Green. The agreement with experiment is made worse.

Rice and Kirkwood (433): By introducing some further approximations, the expression for the viscosity coefficient is written in terms of equilibrium properties of the fluid. The absolute value of the calculated viscosity of argon is still about 50% of the experimental value. This theory was extended to mixtures by Rice and Allnatt (431).

The present status of these theories is reviewed by Collins (95), Green (194, 196), Bondi (56), and Rice and Frisch (432): see also the comments and discussion (21, 110, 132, 133, 134, 135, 195, 253, 337, 342, 370, 371) and similar theories proposed by Eisenschitz and others (100, 102, 103, 131, 136, 241, 382).

A new type of theory, which developed out of Kirkwood's calculation of the friction constant, recently has become fashionable. M. S. Green (198) seems to have been the first to obtain an explicit expression for the viscosity coefficient as an integral of the autocorrelation function of the stress tensor; the quantum-mechanical generalization was given by Mori (362, 363, 364). A simple general derivation, valid for classical multicomponent systems, was given by Kirkwood shortly before his death (272, 274); we refer to several other papers on the subject (197, 199, 217, 218, 221,

286, 343, 365), but we have not listed any of the numerous works on electric and magnetic properties, or articles on the fluctuation-dissipation theorem which do not discuss viscosity in particular.

3. Monatomic Liquid with Solid-like Structure

In these theories it is assumed that each molecule is confined within a fairly small space, and interacts directly only with a few neighbors. Four subspecies may be distinguished: (a) hole theories, (b) vibration theories, (c) phonon theories, (d) relaxation theories. In (a) the liquid is regarded as a lattice with some sites occupied by molecules and others empty. Viscous flow is accomplished by the "jumping" of molecules from one site to another under the influence of an applied force. In (b) the molecule vibrates around an equilibrium position, occasionally transferring momentum to its neighbors. In (c) it is vibrations of the lattice as a whole (sound waves or "phonons") which transmit momentum. In (d) viscous flow is considered similar to the deformation of elastic solids.

It is an unfortunate characteristic of almost all these theories that they manage to introduce one or more "constants" which cannot actually be calculated from molecular data but may be related to macroscopic properties (heat of vaporization, heat of fusion, compressibility, etc.). Ultimately these constants become adjustable parameters chosen to fit experimental data; often the theory has to be "improved" by permitting the constants to vary with temperature and density; and extra factors, taking account of "association," have to be added for liquids which fail to conform to the original formula. Since theories based on assumptions (a), (b), (c), or (d) usually end up with an exponential formula like eq. 5, or something similar to it, the fact that this formula works fairly well for most liquids gives no information about which of the four mechanisms, if any, is correct (*cf.* 340, 341).

The theory of Eyring (142, 143, 166, 180, 406) is the best-known example of type (a); similar theories were proposed by Frenkel (162, 163), Dunn (124), Furth (168, 169), Guareschi (204), Irany (244), and others (8, 9, 26, 32, 33, 34, 219, 240, 267, 280, 330, 384, 453, 473, 534). Many comments and criticisms of the Eyring theory have appeared (6, 9, 28, 46, 55, 69, 97, 116, 125, 140, 141, 146, 179, 201, 202, 228, 231, 258, 298, 304, 340, 355, 359, 361, 378, 415, 416, 417, 518, 522, 527, 529, 548) of which perhaps the most serious is the assertion of Alfrey (6; see also 359) that the hole mechanism cannot describe viscous flow at all, at least in the original form proposed by Eyring.

The theories of Jäger (223, 248a), Sato (452), Andrade (11, 12, 13, 16, 20), Guareschi (203), MacLeod (329) and others (130, 225, 226, 385, 398a, 538) belong to category (b); though once popular they are now out of fashion. The same might be said of category (c),

the phonon theories (60, 61, 63, 64, 70, 408, 413), except that the phonon concept has been reincarnated in recent theories of liquid helium (Section III-D).

Burgers (83, 84) and Partington (397) review the relaxation theories, which continue to be discussed in the more recent literature (277, 278, 359, 366, 373, 458, 514a) perhaps because of the current interest in ultrasonic absorption studies.

4. Semi-empirical Relations with Other Physical Properties; Principles of Corresponding States

Some of the theories mentioned in Section III-A-3 might equally well be classified in this category, the criterion being the extent to which a definite theoretical model of the liquid influences the type of approximations made. Partington (397) has summarized most of the semi-empirical theories published before 1951; we list a few which have appeared since then (9, 17, 41a, 65, 179, 191, 218, 264, 265, 266, 341, 395, 420, 491, 533).

B. FLUCTUATION-DISSIPATION THEORY

While the various theories of viscosity have provided a certain amount of insight into the molecular processes involved in viscous flow, they have not yet satisfied the natural desire for a theoretical explanation of the type which we possess for gas viscosity. The attitude of past theorists seems to have been that it is hopeless to try to understand liquids without first making some rather drastic simplifying assumptions about their structure. Unfortunately the choice of a structure immediately limits the range of flow mechanisms which can be considered. Consequently, while it is possible to discuss the validity of various explanations of the viscosity of a lattice-liquid, it is very difficult to compare them with the results of theories such as have been proposed by Born and Green, or by Kirkwood's group.

Recently a number of theorists have investigated a new approach which may provide a firmer basis for theories of irreversible processes, in the same sense that the method of partition functions provides a common starting-point for equilibrium theories. The new approach will be referred to here as "fluctuation-dissipation theory," though many of the relevant papers do not use this name.

The essential idea used in fluctuation-dissipation theory is that any irreversible process may be viewed as the result of the tendency of a perturbed system to return to equilibrium. Thus viscosity is the measure of the *external* force required to maintain a velocity gradient, and at the same time a measure of the *internal* force which would tend to dissipate that gradient if the external forces were removed. Now it is a consequence of equilibrium statistical mechanics that large fluctuations from uniform conditions occasionally occur, though these fluctuations usually can be neglected

in calculating most equilibrium properties. Suppose we are presented with a system in some non-uniform state, the forces which produce the non-uniformity having been removed an instant earlier, and we are asked to describe the system's return to equilibrium. We do not, in principle, need to know anything about how the system reached its present state, since its future history is completely determined by its present state, and we can therefore treat this as a problem in *equilibrium* statistical mechanics. (It may, of course, be necessary to create a fictitious past history of the system by extrapolating backward in time with the help of the equations of motion, in order to describe the equilibrium fluctuation which would produce the specified non-uniformity.) It remains to be seen how the transport coefficients should be related to the fluctuation properties of an equilibrium system, and how these properties can best be calculated.

It is characteristic of fluctuation-dissipation theory that the various transport coefficients are related to autocorrelation functions of dynamical variables, integrated over a period of time sufficient for the regression of local fluctuations, but short compared to the relaxation time of the entire system, or to the Poincaré recurrence time. The irreversible aspect of the theory is thus clearly related to our concept of irreversible processes in general: If we start with any non-equilibrium state and allow it to decay to equilibrium, it is overwhelmingly probable that the entropy will increase, though if we waited long enough, that non-equilibrium state would ultimately recur and the entropy would return to its original value. (The system is assumed to be confined to a finite volume.) Similarly, the autocorrelation function $S(t)S(0)$ is positive for states separated by a time t so short that they are appreciably correlated. One then expects a long period during which there is no average correlation, and thus no contribution to the integral, so that the integral can be assigned a definite "plateau value." Finally, eons after the experiment has been completed, there is a fluctuation which makes $S(t)S(0)$ negative long enough to cancel out the original positive contribution, and the transport coefficient is thus zero if the integral is extended over infinite time [cf. the discussion by Mazur and Montroll in ref. 338].

A simple example is provided by the diffusion coefficient for a particle performing Brownian motion. We recall that this coefficient is proportional to the mean square displacement of the particle at time t , divided by t ; a quantity which, according to theory, becomes constant after a number of random impulses have been experienced by the particle

$$D = (1/6t)\langle [x(t) - x(0)]^2 \rangle \quad (17)$$

The displacement $x(t)$ may now be expressed in terms

of the initial position $x(0)$ and the velocities of the particle between 0 and t

$$x(t) = x(0) + \int_0^t v(t') dt'$$

so we can write

$$D = (1/6t)\langle \int_0^t v(t') dt' \int_0^t v(t'') dt'' \rangle = (1/6t)\langle \int_0^t dt'' \int_0^t v(t') v(t'') dt' \rangle$$

where the dummy variable t'' has been introduced in order to avoid confusing the variables in the two integrals. The diffusion coefficient of the particle is thus related to an integral over the autocorrelation function $v(t')v(t'')$; the integration over t'' can be taken outside the averaging symbols $\langle \rangle$ since for a stationary process the diffusion constant is independent of time. In Brownian motion theory the velocity is determined by a sequence of random impulses, and D is always positive as can be seen directly from the form of eq. 17. Fluctuation-dissipation theory achieves a similar result for the transport coefficients without having to assume molecular chaos at the beginning.

1. Mathematical Preliminaries

The mathematical techniques used in modern transport theory appear at first sight to be rather esoteric. Closer inspection shows that, while these techniques would indeed be quite difficult to use if one attempted a strict mathematical justification for every step, their practitioners have reduced them to a set of rules for juggling symbols (or "formal manipulation" as it is called). It is taken for granted that if anyone objects to a derivation produced by this method, a mathematician could always be found to prove the same result by more rigorous methods—unless the result is wrong, in which case its falsity will eventually be discovered by comparison with experiment. Often the final result is correct, though obtained by methods which are of dubious validity (42, 150, 460, 492, 493). Furthermore, while such tactics are undoubtedly successful in expediting original research, they are not very suitable when the time comes to explain the results to others.

A common procedure is to represent operators, such as differentiation, by symbols which are manipulated as if they were ordinary algebraic quantities. Suppose Q is the operator d/dx ; it is easy enough to see what Q^2 or Q^n (with n an integer) means, but what about e^{aQ} ? An "exponentiated" operator can be defined by its series expansion

$$e^{aQ} = \sum_{n=0}^{\infty} \frac{Q^n}{n!}$$

and if the operator e^{aQ} is applied to the function $f(x)$, the result is

$$e^{aQ}f(x) = \sum \frac{(aQ)^n}{n!} f(x) = f(x + a)$$

by Taylor's theorem. So e^{aQ} is a "shift" operator which simply translates the argument of the function from x to $x + a$. However, if R is another operator which does not commute with Q (*i.e.*, $QR \neq RQ$), the expression e^{Q+R} is ambiguous and must be defined by a more elaborate procedure (150).

Another useful operator is the one which converts a function $f(x)$ into the number which is its value at the point a , *viz.*, $f(a)$. This operator is written

$$Zf(x) = \int \delta(x - a)f(x)dx = f(a)$$

usually the part $\delta(x - a)$ is written by itself and is called Dirac's delta function. The delta function is called by mathematicians a "distribution" since it is not really a function in the usual sense of the word; it cannot be defined simply by giving its value at every point. It can be considered as the limit of various sequences of functions which are strongly peaked at $x = a$; one may say that $\delta(x - a)$ is zero whenever $x \neq a$, and is infinite at $x = a$ in such a manner that its integral is unity. It is also symmetric, having the property

$$\delta\delta(x - a)/\partial x = -\delta\delta(x - a)\partial a \quad (18)$$

These properties are clearly described rather inadequately by the mere statement that $\delta(x = a)$ is infinite at $x = a$ and zero elsewhere. While it is natural to use the delta function in defining the properties of a system of point masses, some ambiguity arises when one tries to take the square of a delta function. Since Z operates only on functions, not on numbers, an expression like $Z^2f(x)$ is meaningless.

It may be helpful at this point to review the vector and matrix notation used in this article. The expression \mathbf{ab} means the matrix

$$\begin{pmatrix} a_x b_x & a_x b_y & a_x b_z \\ a_y b_x & a_y b_y & a_y b_z \\ a_z b_x & a_z b_y & a_z b_z \end{pmatrix}$$

and is to be distinguished from the scalar product $\mathbf{a} \cdot \mathbf{b}$ which is the trace (sum of the diagonal elements) of that matrix. The operator ∇ is a (symbolic) vector with components $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$; when it acts on a scalar function it is called the gradient. The velocity-gradient tensor $\nabla\mathbf{v}$ (called \mathbf{G} in Section II-B) is represented in this coordinate system by a matrix, as above, whose trace is $\nabla \cdot \mathbf{v}$ (known as the divergence of \mathbf{v}). It is convenient to use the symbols $\nabla\mathbf{r}_i$ and $\nabla\mathbf{p}_i$ which are similar to ∇ except that the differentiations are performed with respect to the position $\mathbf{r}_i = (r_{ix}, r_{iy}, r_{iz})$ or momentum $\mathbf{p}_i = (p_{ix}, p_{iy}, p_{iz})$ of particle i , rather than with respect to a point $\mathbf{r} = (x, y, z)$ in space.

If A is a matrix with components $A_{\alpha\beta}$ and \mathbf{a} is a vector with components a_α (where $\alpha, \beta = 1, 2, 3$), the

product $\mathbf{A} \cdot \mathbf{a}$ is defined as the vector whose components are

$$(\mathbf{A} \cdot \mathbf{a})_\alpha = \sum_\beta A_{\alpha\beta} a_\beta$$

The simple product $\mathbf{A} \cdot \mathbf{B}$ of two matrices A and B is the matrix with components

$$(\mathbf{A} \cdot \mathbf{B})_{\alpha\beta} = \sum_\gamma A_{\gamma\beta} B_{\gamma\alpha}$$

The double product $\mathbf{A}:\mathbf{B}$ is the scalar product, equal to the trace of $\mathbf{A} \cdot \mathbf{B}$

$$\mathbf{A}:\mathbf{B} = \sum_\alpha \sum_\beta A_{\alpha\beta} B_{\beta\alpha}$$

The transpose \mathbf{A}^{tr} of the matrix \mathbf{A} is the matrix with elements

$$A_{\alpha\beta}^{\text{tr}} = A_{\beta\alpha}$$

Any matrix can be decomposed into a symmetrical and an antisymmetrical part

$$\mathbf{A} = \mathbf{A}^{\text{sym}} + \mathbf{A}^{\text{ant}}$$

$$\mathbf{A}^{\text{sym}} = \frac{1}{2}(\mathbf{A} + \mathbf{A}^{\text{tr}})$$

$$\mathbf{A}^{\text{ant}} = \frac{1}{2}(\mathbf{A} - \mathbf{A}^{\text{tr}})$$

When \mathbf{A} is the velocity-gradient tensor $\nabla\mathbf{v}$, the matrix $2(\nabla\mathbf{v})^{\text{ant}}$ is called $\text{rot } \mathbf{v}$ or $\text{curl } \mathbf{v}$ or $\nabla \times \mathbf{v}$. It happens that the antisymmetrical part of a 3×3 matrix has only three independent components, since $A_{\alpha\alpha}^{\text{ant}} = 0$ and $A_{\alpha\beta}^{\text{ant}} = -A_{\beta\alpha}^{\text{ant}}$, and thus students of elementary vector analysis are told that $\text{curl } \mathbf{v}$ is a vector with components $(\text{curl } \mathbf{v})_x = (\partial v_y/\partial z) - (\partial v_z/\partial y)$, etc. Students who take more advanced courses have to unlearn this statement, since $\text{curl } \mathbf{v}$ is not a "real" vector but only a "pseudovector."

In classical viscous flow theory one only needs to use the symmetrical part of $\nabla\mathbf{v}$ provided the motion is "irrotational" ($\text{curl } \mathbf{v} = 0$) and the velocity can be derived from a scalar velocity-potential function ϕ : $\mathbf{v} = \nabla\phi$.

The phase space of an N -body system consists of $6N$ dimensions, one for each coordinate and each momentum component of each particle. The instantaneous state of the system may be represented by a single point in this $6N$ -dimensional space; the "natural motion" of this point is determined by the laws of dynamics. (We are here concerned only with classical mechanics.) A canonical ensemble is a collection of many N -body systems in different states, each represented by a point in phase space; we assume that there are enough points that we may describe their distribution by a continuous function $f(q_1, q_2, \dots, q_{6N})$: the fraction of systems whose representative points lie in the range $(q_1, q_1 + dq_1), \dots, (q_{6N}, q_{6N} + dq_{6N})$ is $f(q_1, \dots, q_{6N}) dq_1 \dots dq_{6N}$. For brevity we write q for all the variables q_1, \dots, q_{6N} .

As the points go through their natural motion, we find that $f(q)$ changes with time, both explicitly and

implicitly. By this is meant that $f(t, q)$ changes its value at a fixed point q , and also changes along the trajectory of natural motion of a representative point because of the variation of the coördinates and momenta of a particular system with time. Liouville's theorem states that the total time-derivative of $f(t, q)$ along a trajectory is zero

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_i \frac{\partial f}{\partial q_i} \frac{\partial q_i}{\partial t} = 0 \quad (19)$$

The quantities $\partial q_i / \partial t$ are of course determined by the laws of motion: The derivative of a coördinate is a velocity, and the derivative of a momentum is a force. Thus Kirkwood (270, 274) writes

$$i \frac{\partial f}{\partial t} + Lf = 0$$

where

$$L = i \sum_i [(p_i/m) \cdot \nabla_{r_i} + (\mathbf{X}_i + \mathbf{F}_i) \cdot \nabla_{p_i}]$$

and the force acting on particle i has been separated into an external force \mathbf{X}_i and a force \mathbf{F}_i due to the other particles in the system. This is the usual definition of the Liouville operator L , the imaginary unit $i = (-1)^{1/2}$ being introduced for mathematical convenience. (It is actually unnecessary for our present purposes.)

2. Determination of the Non-equilibrium Distribution Function

In transport theory it usually is necessary to determine the non-equilibrium distribution function by solving eq. 19 to some approximation; for example, one may try to derive Boltzmann's equation by integrating over the coördinates and momenta of $N - 1$ particles. In fluctuation-dissipation theory this procedure is avoided, and instead the distribution function is expressed as an integral of $S \cdot \nabla \mathbf{v}$ over a period of time sufficient for the dissipation of the fluctuation from the equilibrium state represented by the velocity gradient $\nabla \mathbf{v}$. On calculating the average value of the stress tensor by integrating its product with the distribution function over phase space, one obtains the viscosity coefficients as autocorrelation integrals of the form

$$\eta = (1/VkT) \int_0^{\tau} \langle S_{xy}(t, \mathbf{r}) S_{xy}(0, \mathbf{r}) \rangle dt \quad (20)$$

The exact meaning of such an expression depends on the way in which the stress tensor \mathbf{S} is defined at a point in space (\mathbf{r}) and on the existence of a plateau value for the integral, more or less independent of its upper limit.

Our derivation follows the one recently given by Kirkwood and Fitts (274), with three differences: First, we shall obtain eq. 20 explicitly by using a definition of the stress tensor suggested by Massignon (337); second, we do not include the generalization to multi-component systems and temperature gradients; third,

we do not assume the reader knows any more mathematics than ordinary calculus.

We consider a non-equilibrium system, and describe the deviations from equilibrium by r parameters, $\gamma_1, \dots, \gamma_r$. To calculate the viscosity coefficients one needs only the nine components of the velocity-gradient tensor $\nabla \mathbf{v}$, or more precisely the six independent components of its symmetrical part $(\nabla \mathbf{v})^{sym}$, since we are interested only in irrotational motion. We assume that the system is sufficiently close to equilibrium that we may always discard terms in the distribution function (and in the stress tensor) of higher than first order in the γ 's. This is not an approximation, since the viscosity coefficients are defined by the ratios of the components of the stress and rate-of-deformation tensors when both approach zero.

We write f as the sum of a zero-order distribution function f_0 and a perturbation term f_1 . The former is assumed not to depend explicitly on time ($\partial f_0 / \partial t = 0$) and reduces to f_{eq} when all the γ 's go to zero. The equilibrium distribution function is

$$f_{eq} = A e^{-\beta E(q)}$$

$$E(q) = \sum_i p_i^2 / 2m + \sum_{i \neq j} \sum V_{ij}$$

$$\beta = 1/kT$$

There is some latitude in the choice of f_0 but it turns out to be convenient to choose it to be "locally Maxwellian" having the same form as f_{eq} but with the momenta p_i replaced by

$$p_i' = p_i - m\mathbf{v}(\mathbf{r}_i)$$

where $\mathbf{v}(\mathbf{r}_i)$ is the value of the hydrodynamic velocity at the position of particle i .

The perturbation function f_1 will be of the form

$$f_1 = \sum_j \gamma_j f_{1j}(t, q)$$

according to the assumption that f is linear in the γ 's and reduces to f_{eq} when they vanish.

Substituting $f = f_0 + f_1$ into eq. 19 and using the fact that $\partial f_0 / \partial t = 0$ we obtain

$$Lf_0 + Lf_1 + i(\partial f_1 / \partial t) = Lf_0 + i(df_1 / dt) = 0 \quad (21)$$

This equation is to be solved for f_1 . We are considering a situation in which the velocity gradient has been maintained by appropriate external forces which are suddenly removed at time $t = 0$; it is also assumed that previous to $t = 0$ the distribution function was the "steady-state" function, f_0 , so that $f_1 = 0$ for $t \leq 0$. With this boundary condition we may integrate eq. 21 in the form

$$f_1(t) = -i \int_0^t Lf_0 ds \quad (22)$$

This expression requires some explanation. Let us define, with Kirkwood and Fitts (274), the quantity

$$B(q) = -i(Lf_0(q)/(f_0(q)))$$

If we look at the representative point of a system which is at the phase point q_0 initially, we will find it at a later time s at the point q_s , the relation between q_s and q_0 being determined by the equations of motion. Thus the function $B(q_s)$ is an implicit function of the time variable s .

We shall see that $B(q_s)$ is a linear function of the components of $\nabla\mathbf{v}$ (in fact it can be shown that $B = \beta\mathbf{S}:\nabla\mathbf{v}$, but we have not yet defined \mathbf{S}), and since we need $f_1(t)$ only as far as the terms linear in these components, we can replace f_0 by f_{eq} after operating on f_0 with L

$$Lf_0 \sim Bf_{eq}$$

This is not the same as replacing Lf_0 by Lf_{eq} , since in fact $Lf_{eq} = 0$, and it is $L(f_0 - f_{eq})$ which gives the entire contribution to the integral in eq. 22.

Equation 22 is thus replaced by

$$f_1(t, q_t) = \int_0^t B(q_s)f_0(q_s)ds \quad (23)$$

This result is similar to that obtained by Kirkwood and Fitts, but has been obtained by a simpler method [cf. Edwards and Sanderson (128)]. It is not exactly the same result since we have obtained $f_1(t, q_t)$ by integrating along a trajectory of the natural motion, whereas Kirkwood and Fitts obtained $f_1(t, q)$ by integrating at a fixed point in phase space. The difference has no practical significance since in calculating the viscosity coefficient one integrates over all of phase space anyway.

The quantity $B(q_s)$ which appears in eq. 23 depends on the coordinates and momenta of the individual molecules; since the viscosity coefficient is a relation between functions of points in space, we are not yet ready to use eq. 23.

3. Relation between Microscopic and Macroscopic Variables

The viscosity coefficient appears in a relation between two macroscopic quantities, the stress tensor and the rate-of-deformation tensor. Any theory of viscosity must therefore provide a definition of these tensors in terms of molecular variables. The rate-of-deformation tensor is easily identified with the velocity gradient tensor $\nabla\mathbf{v}$, which is usually considered to be fixed by the conditions of the experiment (cf. eq. 9). The stress tensor is usually defined as a momentum-flux tensor, with a term such as $\sum_i \mathbf{p}_i \mathbf{p}_i / m$ to represent the transport of momentum by molecular motion, plus another term representing the effect of intermolecular forces. While there is no ambiguity in defining such a tensor for a finite region of space, one has to be rather careful in defining its value at a point. If the molecules are regarded as point centers of force, the stress tensor at a fixed point in space would almost always be zero, having a finite value only at occasional instants when

a molecule happened to be at that point. Any useful definition of a stress tensor must therefore be some kind of average, spatial or temporal.

Probability distributions associated with point masses are conveniently described by using the delta function. If the molecule is actually at the point x_0 , the probability that it is in the interval (a, b) is

$$P(a, b) = \int_a^b \delta(x - x_0)dx = \begin{cases} 1 & \text{if } a \leq x_0 \leq b \\ 0 & \text{otherwise} \end{cases} \quad (24)$$

Thus the local mass density might be defined by writing

$$\rho(\mathbf{r}) = m \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \quad (25)$$

an expression which, when integrated over any region V , gives the number of molecules in that region. However, the calculation of fluctuations and correlations requires a knowledge of $\langle \rho^2 \rangle$, and the single spatial integration indicated by $\langle \rangle$ is not sufficient to give a meaning to the terms which involve $[\delta(\mathbf{r}_i - \mathbf{r})]^2$. One must therefore introduce some kind of spatial or temporal coarse-graining in the definition of the density. There is not yet any general agreement on the best way of doing this; Kirkwood (270) prefers temporal coarse-graining, while Massignon (337) has described another procedure in which $\delta(\mathbf{r}_i - \mathbf{r})$ is replaced by a non-singular function of $\mathbf{r}_i - \mathbf{r}$ corresponding to a finite molecular extension. In the sequel we continue to use delta functions with the understanding that they are first to be averaged over space or time before evaluating any expression containing squares of delta functions. For more detailed discussion of this point see Massignon (337).

The time derivative of ρ defined by eq. 25 is determined implicitly by the time-dependence of the coordinates r_i

$$\begin{aligned} \dot{\rho} &= d\rho/dt = \sum_i \left[\frac{\partial}{\partial r_i} \delta(\mathbf{r}_i - \mathbf{r}) \right] \cdot \mathbf{p}_i = \sum_i [\nabla_{r_i} \delta(\mathbf{r}_i - \mathbf{r})] \cdot \mathbf{p}_i \\ &= -\sum_i [\nabla \delta(\mathbf{r}_i - \mathbf{r})] \cdot \mathbf{p}_i = -\nabla \cdot \left[\sum_i \mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{r}) \right] = -\nabla \cdot \mathbf{J} \end{aligned} \quad (26)$$

where we have used the symmetric property of the delta function (eq. 18)

$$\nabla_{r_i} \delta(\mathbf{r}_i - \mathbf{r}) = -\nabla \delta(\mathbf{r}_i - \mathbf{r})$$

and rearranged the expression so as to obtain the momentum density

$$\mathbf{J} = \sum_i \mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{r})$$

The average value of \mathbf{J} is to be identified with the macroscopic mass current which satisfies the continuity equation of hydrodynamics

$$(\partial/\partial t)\langle \rho \rangle + \nabla \cdot \langle \mathbf{J} \rangle = 0 \quad (27)$$

The calculation of the time derivative of \mathbf{J} is not quite as simple, since it depends on the force $\mathbf{F}_{ij} =$

$-\nabla_{\mathbf{r}_i} V_{ij}$ acting between two molecules which are not in general at the same point in space

$$\mathbf{j} = \sum_i \left[(\mathbf{p}_i/m) \cdot \frac{\partial \delta(\mathbf{r}_i - \mathbf{r})}{\partial \mathbf{r}_i} \mathbf{p}_i + \delta(\mathbf{r}_i - \mathbf{r})(\mathbf{X}_i + \sum_{j \neq i} \mathbf{F}_{ij}) \right] \quad (28)$$

In order to define a function of a single point in space we will need to use the Taylor expansion of the delta function. It may be surprising to find that such a singular function can be expanded in a Taylor series, but it is nevertheless true (460).

The first term in eq. 28 may be transformed by using the relation

$$\mathbf{A} \cdot (\mathbf{BC}) = \mathbf{B} \cdot (\mathbf{AC})$$

valid for any three vectors \mathbf{A} , \mathbf{B} and \mathbf{C} , and by using eq. 18

$$\mathbf{p}_i \cdot \nabla_{\mathbf{r}_i} \delta(\mathbf{r}_i - \mathbf{r}) \mathbf{p}_i = \nabla_{\mathbf{r}_i} \delta(\mathbf{r}_i - \mathbf{r}) \cdot (\mathbf{p}_i \mathbf{p}_i) = -\nabla \delta(\mathbf{r}_i - \mathbf{r}) \cdot (\mathbf{p}_i \mathbf{p}_i) \quad (29)$$

The term $\sum \delta(\mathbf{r}_i - \mathbf{r}) \mathbf{X}_i$ is easily interpreted as the external force \mathbf{X} acting on the molecules at \mathbf{r} . This leaves the third term, the sum over the intermolecular forces, to be dealt with.

Using the fact (equality of action and reaction) that $F_{ij} = -F_{ji}$ and introducing the variables $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, we have

$$\sum_i \sum_{j \neq i} \mathbf{F}_{ij} \delta(\mathbf{r}_i - \mathbf{r}) = \frac{1}{2} \sum_i \sum_{j \neq i} \{ \mathbf{F}_{ij} [\delta(\mathbf{r}_i - \mathbf{r}) - \delta(\mathbf{r}_i - \mathbf{r} - \mathbf{r}_{ij})] \} \quad (30)$$

Now expanding $\delta(\mathbf{r}_i - \mathbf{r} - \mathbf{r}_{ij})$ in a Taylor series in powers of \mathbf{r}_{ij} , we have

$$\begin{aligned} \delta(\mathbf{r}_i - \mathbf{r} - \mathbf{r}_{ij}) &= \sum_n \frac{(-\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i - \mathbf{r}})^n}{n!} \delta(\mathbf{r}_i - \mathbf{r}) \\ &= \exp\{-\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i - \mathbf{r}}\} \delta(\mathbf{r}_i - \mathbf{r}) \\ &= \exp\{\mathbf{r}_{ij} \cdot \nabla\} \delta(\mathbf{r}_i - \mathbf{r}) \end{aligned}$$

The right-hand side of eq. 30 thus can be written

$$\begin{aligned} \frac{1}{2} \sum_i \sum_{j \neq i} \mathbf{F}_{ij} (1 - \exp\{\mathbf{r}_{ij} \cdot \nabla\}) \delta(\mathbf{r}_i - \mathbf{r}) &= \\ -\frac{1}{2} \sum_i \sum_{j \neq i} \mathbf{F}_{ij} (\mathbf{r}_{ij} \cdot \nabla) \alpha(\mathbf{r}_{ij} \cdot \nabla) \delta(\mathbf{r}_i - \mathbf{r}) &= \\ \nabla \cdot \left\{ -\frac{1}{2} \sum_i \sum_{j \neq i} (\mathbf{r}_{ij} \mathbf{F}_{ij}) \alpha(\mathbf{r}_{ij} \cdot \nabla) \delta(\mathbf{r}_i - \mathbf{r}) \right\} \end{aligned} \quad (31)$$

where the operator function α is defined by

$$\alpha(x) = \frac{e^x - 1}{x} = 1 + \frac{1}{2}x + \dots = \sum_{p=0}^{\infty} \frac{x^p}{(p+1)!}$$

We can now define a momentum-current tensor π

$$\begin{aligned} \pi &= \pi_K + \pi_V \quad (32) \\ \pi_K &= \sum_i (\mathbf{p}_i \mathbf{p}_i / m) \delta(\mathbf{r}_i - \mathbf{r}) \\ \pi_V &= -\frac{1}{2} \sum_i \sum_{j \neq i} (\mathbf{r}_{ij} \mathbf{F}_{ij}) \alpha(\mathbf{r}_{ij} \cdot \nabla) \delta(\mathbf{r}_i - \mathbf{r}) \end{aligned}$$

which satisfies the equation

$$\mathbf{j} = -\nabla \cdot \pi + \mathbf{X} \quad (33)$$

When one multiplies eq. 33 by f and integrates over the \mathbf{r} 's and \mathbf{p} 's one gets a similar equation for the average values

$$\langle \mathbf{j} \rangle = -\nabla \cdot \langle \pi \rangle + \langle \mathbf{X} \rangle \quad (34)$$

We have given here the exact expression for π_V derived by Massignon (sec. 8 of ref. 337); Kirkwood and others consider it sufficiently accurate to replace α by 1, an approximation valid for short-range forces.

The local hydrodynamic velocity \mathbf{v} , which already has been introduced as an externally fixed parameter, now can be related to the momentum density and mass density defined in terms of molecular variables

$$\langle \mathbf{j} \rangle = \langle \rho \rangle \mathbf{v} \quad (35)$$

We can choose a pressure tensor having the same form as π , with the momenta \mathbf{p}_i replaced by $\mathbf{p}_i - m\mathbf{v}$, thus

$$\mathbf{P} = \langle \pi \rangle - \langle \rho \rangle \mathbf{v} \mathbf{v} = \mathbf{P}_K + \mathbf{P}_V \quad (36)$$

$$\mathbf{P}_K = \langle \pi_K \rangle - \langle \rho \rangle \mathbf{v} \mathbf{v} = \left\langle \sum_i m^{-1} (\mathbf{p}_i - m\mathbf{v})(\mathbf{p}_i - m\mathbf{v}) \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle$$

$$\mathbf{P}_V = \langle \pi_V \rangle$$

In macroscopic hydrodynamics the viscosity coefficients η and λ are defined as the coefficients of the symmetrical part and the divergence, respectively, of the rate-of-deformation tensor, provided the pressure tensor can be expressed in the form

$$\mathbf{P} = P_0 \mathbf{1} - 2\eta (\nabla \mathbf{v})^{sym} - \lambda (\nabla \cdot \mathbf{v}) \mathbf{1} \quad (37)$$

We can thus find the appropriate microscopic definitions of η and λ by expressing \mathbf{P} as an average of the stress tensor using the non-equilibrium distribution function f already determined.

Recalling that f has been expressed as a sum of f_0 and f_1 , we can write the average of any quantity S in the form

$$\langle S \rangle = \langle S \rangle_0 + \langle S \rangle_1$$

When S is the pressure tensor defined above, $\langle S \rangle_0$ must be simply the local equilibrium pressure P_0 which is unaffected by the presence of a local velocity \mathbf{v} , provided the variation of \mathbf{v} over a very small but macroscopic region of space can be ignored. The effects of viscosity are all contained in $\langle S \rangle_1$, which is an average calculated with the perturbation function f_1 defined by eq. 23.

The remainder of the derivation consists of showing that $B = \beta S : \nabla \mathbf{v}$, sorting out the various components of the pressure tensor, showing that terms like $S_{xy} S_{xx} - (\nabla \mathbf{v})_{xx}$ (which arise from substituting the value of f_1 according to eq. 23) vanish on integrating over all the momenta, and only terms like $S_{xx} S_{xx} (\nabla \mathbf{v})_{xx}$ and $S_{xy} S_{xy} (\nabla \mathbf{v})_{xy}$ remain. The reader will only be convinced of this if he works it out himself. The result is that in an isotropic fluid the coefficient η is equal to the integral of the autocorrelation function of any off-diagonal component of S

$$\eta = (\beta/V) \int_0^\tau \langle S_{xy}(t, r) S_{xy}(0, r) \rangle dt \quad (20)$$

and the bulk viscosity is similarly related to the diagonal components

$$\kappa = \lambda + \frac{2}{3} \eta = (\beta/V) \int_0^\tau \langle S_{xx}(t, r) S_{xx}(0, r) \rangle dt \quad (38)$$

One could also write κ as the sum of three integrals over the autocorrelation functions of S_{xx} , S_{yy} and S_{zz} , divided by three, and similarly for η .

We now review the approximations used in deriving eq. 20 and 38. First, we dropped terms non-linear in the velocity gradient several times; these can be retained if one wants to describe non-Newtonian flow, but little progress has been made along this line so far although a general expression could be written down. Second, we have not proved that the integral of $\langle S(t)S(0) \rangle$ really has a plateau value independent of its upper limit τ , although this seems a plausible assumption. Third, it should be remembered in doing actual calculations that the delta functions must be "smeared out" by spatial or temporal coarse-graining before integrating over phase space. Fourth, the replacement of the operator $\alpha(\mathbf{r}_{ij} \cdot \nabla)$ by unity in the potential part of \mathbf{S} is valid only when the dominant contribution to the viscosity comes from the short-range forces. Finally, it should again be emphasized that $\langle \rangle$ means an average over *all* states of an equilibrium ensemble, including the fluctuations which give rise to macroscopic velocity gradients, and may not be approximated, as is sometimes done in other problems, by assuming that the system is always in its "most probable" state. With these reservations, it is fair to say that eq. 20 and 38 are exact expressions for the viscosity coefficients of a fluid. They do not depend on any assumptions about the structure of the fluid except those which are completely consistent with our present state of knowledge—*i.e.*, that velocity gradients not maintained by external forces *are* dissipated by viscous forces, and that small regions of the fluid quickly reach local equilibrium in the presence of a hydrodynamic velocity whose variation is significant only over large distances.

The question now arises, is a fluctuation-dissipation formula of any practical use? While it may be a "formal" solution of the problem, it appears that one needs to know quite a lot about molecular motions in order to evaluate such an autocorrelation integral. The situation is not any better than in equilibrium theory, where exact solutions are impossible except in a few special cases; and one can hardly expect to be able to calculate the viscosity of a real liquid when one cannot yet calculate its heat capacity or compressibility without making drastic approximations.

Nevertheless, it is encouraging to find that the new theory can yield all the exact results previously obtained by kinetic-theory methods, and offers a possible method for tackling problems for which the older

methods are completely inadequate. Mori (363) (see also H. S. Green (197)) has shown that for dilute gases the autocorrelation formula reduces to the Chapman-Enskog (binary collision) results; recently it has been shown (553) that Enskog's results for a dense fluid of hard spheres also can be derived from the formula. It can be seen easily that eq. 20 has the same form as eq. 15 by writing $\mathbf{S} = \mathbf{S}_K + \mathbf{S}_V$ and expanding the product $S(t)S(0)$ into a sum of three terms. The first term, $\int \langle S_K(t)S_K(0) \rangle dt$, is the contribution from momentum transport by molecular motion, and reduces to eq. 3 in the low-density limit. (One assumes an exponential autocorrelation function with no correlation between successive collisions, as in the kinetic theory.) The other terms describe the contribution from momentum transport at collisions. While the force between two hard spheres is either zero or infinite depending on whether they are in contact, the time integral of the force over a short time during which a collision takes place is just the momentum change at that collision. It can be shown that the three terms depend on the collision rate exactly as indicated in eq. 15, although it is considerably more difficult to prove that the numerical constants are the ones found by Enskog. This can be done, but the details of the calculation have not yet been published.

The autocorrelation integral also can be evaluated by the method of molecular dynamics, invented by Alder and Wainwright (2, 3, 4, 5, 531). An electronic computer was used to solve the equations of motion for a few hundred particles, and detailed records of all positions and velocities are thus available for systems of various densities over periods of time corresponding to hundreds of thousands of collisions. The particles have a hard-sphere repulsive interaction, and in some cases a "square-well" attractive force has been added. It would be possible to deal with more complicated forces, but with these simple models one can simulate many properties of real substances. A calculation of the diffusion constant, using the autocorrelation formula, already has been published (2, 531), and work on the viscosity coefficient is now in progress (79).

C. QUANTUM-MECHANICAL GENERALIZATION

While one might get the impression, from reading discussions of the "rate theory" of viscosity, that viscous flow is necessarily a quantum-mechanical process, involving transition states or tunneling through potential barriers, there is little direct evidence that quantum-mechanical effects are important in liquids at room temperature. Only in the case of helium, at temperatures near absolute zero, is it certain that any theory based on classical mechanics must fail to describe viscous behavior. One of the quantum theories constructed to explain the properties of liquid helium will be discussed in the next section; here we must add a

brief note on the quantum-mechanical generalization of fluctuation-dissipation theory.

Mori (364) has shown that for a quantum system the viscosity coefficient is formally equal to

$$\eta = (1/V) \int_0^\tau ds \int_0^\beta \langle S_{xy}(s + i\hbar\lambda) S_{xy}(0) \rangle d\lambda \quad (39)$$

where \hbar is Planck's constant divided by 2π . His proof depends on finding the perturbation of the quantum-mechanical density operator by a procedure similar to that used by Kirkwood and Fitts (274) to find the perturbation of the classical distribution function. The physical meaning of the result is not as clear since it involves the value of the stress tensor at a complex time ($s + i\hbar\lambda$). Equation 20 is recovered easily as the classical limit by letting \hbar go to zero; and if one expands $S_{xy}(s + i\hbar\lambda)$ as a Taylor series in powers of $i\hbar\lambda$, one can see that the magnitude of the quantum-mechanical correction increases with β ($= 1/kT$) and becomes dominant at low temperatures. Montroll and Ward (356, 358) have proposed a method for evaluating expressions like eq. 39 using diagrams similar to those introduced by Feynman in quantum electrodynamics, but taking account of the complex time variable. At this writing, no explicit results for the viscosity coefficient based on eq. 39 have been published.

D. QUANTUM HYDRODYNAMICS (LANDAU-KHALATNIKOV THEORY)

It is now generally recognized that the peculiar viscous behavior of helium at temperatures near absolute zero is not merely a curiosity of interest only to specialists in low-temperature physics. Rather it is, for viscous flow theory, the "exception which proves the rule," in the deepest sense of that expression. The relation between theory and experience cannot be comprehended fully unless one knows at just what point the physical postulates of the theory must become false. One does not have to be able to integrate the equations of motion of classical mechanics in order to conclude that no theory based on those equations can describe liquid helium.

We can hardly do justice here to the many theories proposed to explain superfluidity, and therefore we select for consideration, rather arbitrarily, just one of them: the Landau-Khalatnikov (L.K.) theory (261, 262, 263, 293, 294, 295, 296). To justify this choice it could be said that this theory seems to have been developed more intensively, and to have yielded more definite predictions capable of experimental verification, than any other. While its results frequently are referred to, the L.K. theory itself has not been sufficiently discussed, except in Russia. English translations of the basic papers exist, but do not seem to be universally accessible.

In his first paper in 1941, Landau proposed to explain the properties of liquid helium as a consequence of the limited nature of the collective motions or "excitations" permitted to the system at low temperatures (293). In order to give a precise description of these collective excitations, he treated the macroscopic hydrodynamic variables—density and velocity—as quantum-mechanical operators, instead of applying quantum mechanics to the motions of the individual particles. While the quantization procedure was carried out by *analogy* with particle quantum mechanics, quantum hydrodynamics was not *deduced* from a "more fundamental" hypothesis; it must be considered as a new set of postulates, which can only be justified by comparing its consequences with experiment. Thus Landau was able to predict the phenomenon of "second sound" (thermal waves), previously predicted by Tisza, and confirmed experimentally by Peshkov in 1944. Landau also predicted that at absolute zero the velocity of propagation of second sound would equal that of ordinary sound divided by $\sqrt{3}$, a prediction not yet conclusively tested. Landau and Khalatnikov attempted a quantitative calculation of the viscosity coefficient in 1949 (295, 296), and were able to reach some definite conclusions about the temperature dependence (*vide infra*).

The basic excitations in the L.K. theory are "phonons" and "rotons." (The Onsager-Feynman vortex filaments also have been incorporated in some recent papers (309, 404).) The phonons are simply quantized sound waves or density fluctuations, similar to photons in the quantum theory of the electromagnetic field. The exact nature of rotons is a subject of some controversy; they may be described as some kind of local vortex motion (154, 155, 284, 323, 419). In the L.K. theory, rotons are short-wave excitations characterized by a certain relation between energy and momentum, and they merge continuously into the long-wave phonons, although in Landau's earlier paper (293) there appeared to be a sharper distinction between phonons and rotons.

Quantum hydrodynamics is similar to quantum field theory, but it should be remembered that this is vintage-1941 quantum field theory, a rather mild variety compared to some of the exotic brews we have seen in recent years. In fact, it can be understood by anyone who is familiar with elementary quantum mechanics, as expounded in a textbook such as Schiff's. (For a more detailed exposition of quantum hydrodynamics we refer to London's book (322).)

For the local mass density operator we can use the function $\rho(\mathbf{R})$ already defined by eq. 25

$$\rho(\mathbf{R}) = m \sum_i \delta(\mathbf{r}_i - \mathbf{R}) \quad (25)$$

since for a single particle described by a wave function $\psi(\mathbf{r})$ the probability of finding that particle at the

point \mathbf{R} is

$$\langle \rho(\mathbf{R}) \rangle = \int \psi^*(\mathbf{r}) \rho(\mathbf{R}) \psi(\mathbf{r}) d\mathbf{r} = m \int \psi^*(\mathbf{r}) \delta(\mathbf{r} - \mathbf{R}) \psi(\mathbf{r}) d\mathbf{r} = m \psi^*(\mathbf{R}) \psi(\mathbf{R}) = m |\psi(\mathbf{R})|^2$$

The symbol $\langle \rangle$ now indicates the quantum-mechanical expectation value of an operator.

The quantum-mechanical operator for the momentum of particle i is $\mathbf{p}_i = \hbar(-1)^{1/2} \Delta_{\mathbf{r}_i}$, and one might expect to be able to define a momentum-density operator by multiplying \mathbf{p}_i by $\delta(\mathbf{r}_i - \mathbf{R})$ and summing over all the particles. However, $\mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{R})$ is no longer the same as $\delta(\mathbf{r}_i - \mathbf{R}) \mathbf{p}_i$ since \mathbf{p}_i and \mathbf{r}_i are non-commuting operators. It turns out to be consistent to define

$$\mathbf{J}_i = \frac{1}{2} [\mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{R}) + \delta(\mathbf{r}_i - \mathbf{R}) \mathbf{p}_i]$$

thus

$$\langle \mathbf{J}_i \rangle = \frac{1}{2} \hbar (-1)^{-1/2} \int \psi^* \nabla \delta(\mathbf{r}_i - \mathbf{R}) \psi d\mathbf{r}_i + \frac{1}{2} \hbar (-1)^{-1/2} \int \psi^* \delta(\mathbf{r}_i - \mathbf{R}) \nabla \psi d\mathbf{r}_i$$

Integrating by parts in the first term, we get

$$\langle \mathbf{J}_i \rangle = \frac{1}{2} \hbar (-1)^{-1/2} \{ \psi^*(\mathbf{R}) \nabla \psi(\mathbf{R}) - \psi(\mathbf{R}) \nabla \psi^*(\mathbf{R}) \}$$

The total momentum-density operator is

$$\mathbf{J}(\mathbf{R}) = \sum_i \mathbf{J}_i(\mathbf{R})$$

The local velocity is similarly represented, not by $\rho^{-1} \mathbf{J}$ or $\mathbf{J} \rho^{-1}$ but by

$$\mathbf{v} = \frac{1}{2} (\rho^{-1} \mathbf{J} + \mathbf{J} \rho^{-1})$$

Following Landau's notation (293) we shall henceforth use ρ_1 and \mathbf{v}_1 to denote the density and velocity operators at the point \mathbf{R}_1 in space, rather than the operators associated with particle one; and having defined these operators we can forget about the atomic constitution of the fluid and treat it as a continuum.

We now need the commutation rules for ρ and \mathbf{v} . These are calculated easily and the results are

$$\rho_1 \rho_2 - \rho_2 \rho_1 = 0 \quad (40)$$

$$\mathbf{v}_1 \rho_2 - \rho_2 \mathbf{v}_1 = \hbar (-1)^{-1/2} \nabla \delta(\mathbf{R}_1 - \mathbf{R}_2) \quad (41)$$

$$\mathbf{v}_1 \mathbf{v}_2 - \mathbf{v}_2 \mathbf{v}_1 = \hbar (-1)^{-1/2} \delta(\mathbf{R}_1 - \mathbf{R}_2) \rho_1^{-1} \text{curl } \mathbf{v} \quad (42)$$

$$(\text{curl } \mathbf{v})_1 \rho_2 - \rho_2 (\text{curl } \mathbf{v})_1 = 0 \quad (43)$$

Note that in eq. 42 one can use either ρ_1^{-1} or ρ_2^{-1} on the right-hand side because of the delta function; and that in eq. 43, $(\text{curl } \mathbf{v})_1$ means the tensor operator $\text{curl } \mathbf{v}$ at the point 1 in space.

Landau now points out that if $\langle \text{curl } \mathbf{v} \rangle = 0$ at every point in space at any time, then $\text{curl } \mathbf{v}$ commutes with ρ , \mathbf{v} and the Hamiltonian and therefore remains zero at all subsequent times. This "irrotational" state of motion is thus a stationary state of the system; and he argues that there are no states with non-zero but infinitesimally small values of $\text{curl } \mathbf{v}$. There is of course a whole spectrum of states with finite values of $\text{curl } \mathbf{v}$, but there must be an "energy gap" Δ separating them

from the lowest irrotational state. Of course for any real liquid the lowest rotational states may have either higher or lower energy than the lowest irrotational states; Δ may be either positive or negative. The value of Δ cannot be calculated from such a macroscopic theory, but must be taken as a parameter fixed by experiment. In the case of liquid helium, it is consistent to assume that Δ is positive, so that the motion is irrotational at very low temperatures; it is known by experiment that liquid helium can flow through very thin tubes with no resistance, and therefore the usual mechanism of energy dissipation by excitation of internal motions somehow fails to operate. The absence of friction is explained by invoking the quantum concept that a system cannot absorb a certain amount of energy unless that amount is sufficient to raise it to one of its excited states.

After Landau's theory was published, the criticism was made that it did not really explain *why* there happens to be such a scarcity of low-lying excited states in liquid helium; this could only be explained by considering the actual nature of helium atoms (152, 154). There seemed to be no reason why the isotope ^3He should not have the same superfluid properties as ^4He if Landau's theory was correct; whereas the atomic theories could take into account the fact that ^3He obeys Fermi-Dirac statistics while ^4He obeys Bose-Einstein statistics. With these criticisms in mind, let us continue with Landau's theory.

From a macroscopic point of view, the energy per unit volume of a liquid is $\frac{1}{2} \rho v^2 + \rho \epsilon(\rho)$ where the internal energy ϵ is some function of the density. Taking into account the fact that ρ and \mathbf{v} at the same point do not commute, we can write the corresponding quantum-mechanical Hamiltonian operator as $\frac{1}{2} \mathbf{v} \cdot \rho \mathbf{v} + \rho \epsilon(\rho)$, and the total Hamiltonian as

$$H = \int \{ \frac{1}{2} \mathbf{v} \cdot \rho \mathbf{v} + (\rho) \rho \epsilon \} d\mathbf{r} \quad (44)$$

In order to reproduce the equations of hydrodynamics with our quantized density and velocity operators, we use the rule that the time derivative of an operator is determined by its commutator with the Hamiltonian

$$\begin{aligned}](\rho_1) &= [i/\hbar H \rho - \rho H] \\ &= [i/\hbar] \int \frac{1}{2} [\mathbf{v}_2 \cdot \rho_2 (\mathbf{v}_2 \rho_1 - \rho_1 \mathbf{v}_2) + (\mathbf{v}_2 \rho_1 - \rho_1 \mathbf{v}_2) \cdot \rho_2 \mathbf{v}_2] d\mathbf{r} \\ &= \int \nabla \delta(\mathbf{R}_2 - \mathbf{R}_1) \cdot \mathbf{J}_2 d\mathbf{R}_2 \\ &= - \int \delta(\mathbf{R}_2 - \mathbf{R}_1) \nabla \cdot d\mathbf{R}_2 \\ &= - \nabla \cdot \mathbf{J}_1 \end{aligned}$$

(Terms involving $\epsilon(\rho)$ vanish because ρ_1 and ρ_2 commute everywhere.) Thus we have the continuity equation in operator form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \frac{1}{2} (\rho \mathbf{v} + \mathbf{v} \rho) = 0$$

and similarly one can obtain Euler's equation in the form

$$\frac{\partial \mathbf{v}}{\partial t} + \frac{1}{2}(\mathbf{v} \cdot \nabla) \mathbf{v} + \frac{1}{2}(\nabla \cdot \mathbf{v}) \mathbf{v} = -\rho^{-1} \nabla \frac{d\epsilon}{d\rho}$$

where $d\epsilon/d\rho$ is the pressure.

Any function describing the density of the liquid can be expanded in a Fourier series of the form

$$\rho(\mathbf{r}) = \rho_0 + V^{-1/2} \sum_{\mathbf{k}} \{ \rho_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} + \rho_{\mathbf{k}}^* e^{-i\mathbf{k} \cdot \mathbf{r}} \} \quad (45)$$

where $\rho_0 = Nm/V$ is the equilibrium average density. The same expansion can be used when ρ and \mathbf{v} are quantum-mechanical operators; each term in the sum can then be associated with a phonon of momentum $\mathbf{p} = \hbar\mathbf{k}$, representing a sound wave of frequency $\omega = c\hbar k$ traveling at a velocity c .

The commutation rules for the operators $\rho_{\mathbf{k}}$ and $\mathbf{v}_{\mathbf{k}}$, which we now call $\rho_{\mathbf{p}}$ and $\mathbf{v}_{\mathbf{p}}$ following Landau and Khalatnikov, are determined by substituting eq. 45 and 46 into eq. 41 and using the Fourier expansion of the delta function

$$\delta(\mathbf{r}_1 - \mathbf{r}_2) = \frac{1}{2} V^{-1/2} \sum_{\mathbf{k}} \{ e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} + e^{-i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \} \quad (46)$$

In order that eq. 41 may be satisfied as an identity for all values of \mathbf{r}_1 and \mathbf{r}_2 , the coefficients of corresponding exponentials on the left and right sides of the equation must be equal, and this gives the results

$$\begin{aligned} \rho_{\mathbf{p}} \rho_{\mathbf{s}}^* - \rho_{\mathbf{s}}^* \rho_{\mathbf{p}} &= (\rho_0 p / 2c) \delta_{\mathbf{p}\mathbf{s}} \\ \mathbf{v}_{\mathbf{p}} &= (c\mathbf{p} / \rho_0 p) \rho_{\mathbf{p}} \end{aligned} \quad (47)$$

where $\delta_{\mathbf{p}\mathbf{s}}$ is the Kronecker delta symbol, equal to one if $\mathbf{p} = \mathbf{s}$ and to zero if $\mathbf{p} \neq \mathbf{s}$.

If we now substitute the Fourier expansions of ρ and \mathbf{v} into the term $(1/2)\mathbf{v} \cdot \rho \mathbf{v}$ in eq. 44 and integrate over the volume of the liquid, we find that the result can be written in the form

$$\begin{aligned} H &= H_0 + V_3 + V_4 \\ H_0 &= (c^2 / \rho_0) \sum_{\mathbf{p}} (\rho_{\mathbf{p}} \rho_{\mathbf{p}}^* + \rho_{\mathbf{p}}^* \rho_{\mathbf{p}}) \end{aligned} \quad (48)$$

where V_3 and V_4 are sums of products of three and four of the ρ 's, respectively.

Equation 48 is essentially the Hamiltonian for a system of harmonic oscillators, whose properties are well known. $\rho_{\mathbf{p}}^*$ and $\rho_{\mathbf{p}}$ can be related to operators which create and annihilate phonons of momentum \mathbf{p}

$$\rho_{\mathbf{p}}^* = a_{\mathbf{p}}^+ e^{-i\omega t} (\rho_0 p / 2c)^{1/2}, \quad \rho_{\mathbf{p}} = a_{\mathbf{p}} e^{i\omega t} (\rho_0 p / 2c)^{1/2} \quad (49)$$

where

$$\omega = cp/\hbar$$

Substituting eq. 49 into eq. 48, we obtain

$$H_0 = \sum (a_{\mathbf{p}} a_{\mathbf{p}}^+ + a_{\mathbf{p}}^+ a_{\mathbf{p}}) (\hbar\omega/2) \quad (50)$$

Instead of using wave functions, we define a state of the system by specifying the number of phonons present in each momentum state \mathbf{p} . A state with $n_{\mathbf{p}}$ phonons in

state \mathbf{p} is denoted by Dirac's ket symbol, $|\dots n_{\mathbf{p}} \dots\rangle$ where " \dots " indicates the occupation numbers of the other states, not specified. When $a_{\mathbf{p}}^+$ operates on a state with $n_{\mathbf{p}}$ phonons on momentum \mathbf{p} , it changes it to a state with $n_{\mathbf{p}} + 1$ phonons of momentum \mathbf{p} , a state represented symbolically by the equation

$$a_{\mathbf{p}}^+ |\dots n_{\mathbf{p}} \dots\rangle = (n_{\mathbf{p}} + 1)^{1/2} |\dots n_{\mathbf{p}} + 1 \dots\rangle \quad (51)$$

Similarly the annihilation operator $a_{\mathbf{p}}$ reduces by one the number of phonons with momentum \mathbf{p}

$$a_{\mathbf{p}} |\dots n_{\mathbf{p}} \dots\rangle = (n_{\mathbf{p}})^{1/2} |\dots n_{\mathbf{p}} - 1 \dots\rangle \quad (52)$$

The factors $(n_{\mathbf{p}} + 1)^{1/2}$ and $(n_{\mathbf{p}})^{1/2}$ have been included in the definitions of $a_{\mathbf{p}}^+$ and $a_{\mathbf{p}}$ so that the product $a_{\mathbf{p}}^+ a_{\mathbf{p}}$ will have the convenient property

$$a_{\mathbf{p}}^+ a_{\mathbf{p}} |\dots n_{\mathbf{p}} \dots\rangle = n_{\mathbf{p}} |\dots n_{\mathbf{p}} \dots\rangle \quad (53)$$

thus $a_{\mathbf{p}}^+ a_{\mathbf{p}}$ is the "number operator" which, operating on a state, brings out as a factor the number of phonons of momentum \mathbf{p} in that state. Conversely

$$a_{\mathbf{p}} a_{\mathbf{p}}^+ |\dots n_{\mathbf{p}} \dots\rangle = (n_{\mathbf{p}} + 1) |\dots n_{\mathbf{p}} \dots\rangle \quad (54)$$

and combining eq. 53 and 54 we recover the commutation rule, eq. 47

$$a_{\mathbf{p}} a_{\mathbf{p}}^+ - a_{\mathbf{p}}^+ a_{\mathbf{p}} = 1$$

($a_{\mathbf{p}}$ commutes with $a_{\mathbf{p}'}$ and $a_{\mathbf{p}'}^+$, if $\mathbf{p} \neq \mathbf{p}'$.)

When H_0 operates on any state $|\dots\rangle$ the result is

$$H_0 |\dots\rangle = [\sum (n_{\mathbf{p}} + 1/2) \hbar\omega] |\dots\rangle$$

and we can therefore write H_0 symbolically in the form

$$H_0 = \sum (n_{\mathbf{p}} + 1/2) \hbar\omega \quad (55)$$

which is the familiar expression for the energy of a system of independent harmonic oscillators, including the zero-point energy. The "matrix elements" of the operators $a_{\mathbf{p}}$ and $a_{\mathbf{p}}^+$ are

$$(a_{\mathbf{p}})_{n'n} = \langle n' | a_{\mathbf{p}} | n \rangle = (n_{\mathbf{p}} + 1)^{1/2} \delta_{n_{\mathbf{p}}+1, n_{\mathbf{p}}}, \quad n_{\mathbf{p}'} = (a_{\mathbf{p}}^+)_{n',n} \quad (56)$$

where n stands for the set of occupation numbers and differs from n' only in the occupation number of the momentum state \mathbf{p} . Equation 56 follows from eq. 51 and 52 and the orthonormality condition

$$\langle n' | n \rangle = \delta_{n_{\mathbf{p}}, n_{\mathbf{p}'}}$$

To calculate the viscosity coefficient, Landau and Khalatnikov (295, 296) introduced the approximation of treating the phonon and roton excitations as an ideal gas of quasi-particles, applying the kinetic theory to compute the transport of momentum in the binary collision approximation. One might think that this would lead to a viscosity coefficient increasing with temperature, as in a gas, contrary to the experimental evidence which indicates a negative temperature coefficient below 1.6°K. (We refer here to the viscosity as measured by the disk experiments, rather than by capillary flow measurements.) However, it turns out that the effective cross section (and thus the mean free

path) for phonon-phonon scattering is strongly temperature dependent, and hence the L.K. theory is able to give a fairly convincing qualitative explanation of the temperature variation of the viscosity coefficient at temperatures well below the lambda point.

The interaction between phonons is determined by the terms V_3 and V_4 in the Hamiltonian. We consider the scattering of phonons with momenta \mathbf{p} and \mathbf{p}_1 , resulting in phonons with momenta \mathbf{p}' and \mathbf{p}_1' after the collision. The term V_3 , which contains products of three annihilation or creation operators, cannot give a direct contribution to this process in first-order perturbation theory, since it must change a state with an even number of phonons to one with an odd number of phonons, and conversely. V_4 contains products of four operators, and we are interested, in particular, in terms like $a_{\mathbf{p}'}^+ a_{\mathbf{p}'}^+ a_{\mathbf{p}} a_{\mathbf{p}_1}$. This operator annihilates a phonon of momentum \mathbf{p}_1 and one of momentum \mathbf{p} , and then creates one of momentum \mathbf{p}_1' and one of momentum \mathbf{p}' . V_4 will contain other terms in which these same operators appear in a different order, but one can rearrange them by using the commutation rules.

Term V_3 gives a second-order contribution to the scattering process, since it can induce transitions from the initial state (A) to a virtual intermediate state (I) and then to the final state (F). There are six possible kinds of intermediate states; we denote by Y_{Ai} the combination of operators which produces the state i from the initial state A containing two phonons of momenta p and p_1 ; Y_{iF} converts this state to the final state F, with two phonons of momenta p' and p_1' . Note that momentum but not energy is conserved in the intermediate state.

Intermediate state and phonon momenta

	$\mathbf{p} + \mathbf{p}_1$			
I	$\mathbf{p} + \mathbf{p}_1$			
II	$\mathbf{p} - \mathbf{p}'$	\mathbf{p}_1	\mathbf{p}'	
III	$\mathbf{p} - \mathbf{p}_1'$	\mathbf{p}_1	\mathbf{p}_1'	
IV	$\mathbf{p}_1 - \mathbf{p}_1'$	\mathbf{p}	\mathbf{p}_1'	
V	$\mathbf{p}_1 - \mathbf{p}'$	\mathbf{p}	\mathbf{p}'	
VI	$\mathbf{p} \quad \mathbf{p}_1$	\mathbf{p}'	\mathbf{p}_1'	$-\mathbf{p}' - \mathbf{p}_1'$

According to quantum-mechanical scattering theory, the effective differential cross section is

$$d\sigma(\mathbf{p}, \mathbf{p}_1, \mathbf{p}', \mathbf{p}_1') = (hc)^{-1} |H_{AF}'|^2 \delta(\epsilon + \epsilon_1 - \epsilon' - \epsilon_1') h^{-3} d\mathbf{p}' \quad (57)$$

where, in the approximation used in the L.K. theory

$$H'_{AF} = \sum_{i=I}^{VI} \frac{(V_3)_{Ai} (V_3)_{iF}}{E_A - E_i} + (V_4)_{AF} \quad (58)$$

and the matrix elements $(V_3)_{Ai}$, $(V_3)_{iF}$ and $(V_4)_{AF}$ are to be computed using eq. 48 and 56 together with some empirical information about $\epsilon(\rho)$ obtained from the compressibility of the liquid. ϵ , ϵ_1 , ϵ' and ϵ_1' are the energies for phonons of momenta \mathbf{p} , \mathbf{p}_1 , \mathbf{p}' and \mathbf{p}_1' , respectively.

The denominators in eq. 58 depend on the energy-momentum relation for phonons. The energy of a free phonon is $\hbar\omega = cp$, according to eq. 55, but we cannot use this relation in eq. 58 because the denominators of the first five terms in the sum would be zero. To avoid getting an infinite result for H_{AF}' Landau and Khalatnikov combine the phonons and rotons to obtain a single energy-momentum spectrum. They assume that for small \mathbf{p} the energy is proportional to \mathbf{p} , and for larger momenta it falls back to a minimum value Δ at $\mathbf{p} = \mathbf{P}_0$. The rotons have an energy

$$E = \Delta + (\mathbf{p} - \mathbf{P}_0)^2 / 2\mu$$

where μ is the "effective mass" of a roton, a parameter to be determined from experiments like Δ and P_0 . (This can be done by fitting the specific heat curve or, more directly, from neutron scattering experiments.)

The combined spectrum is assumed to have the form

$$\epsilon^2 = A_1 p^2 + A_2 p^4 + A_3 p^6 + A_4 p^8$$

where the constants A_1 to A_4 are determined by the conditions

$$\begin{aligned} (\partial\epsilon/\partial p)_{p=0} &= c; & (\partial\epsilon/\partial p)_{p=P_0} &= 0; \\ (\partial^2\epsilon/\partial p^2)_{p=P_0} &= \mu^{-1}; & (P_0) &= \Delta \end{aligned}$$

The values of the A 's are thus found to be

$$A_1 = c^2; \quad A_2 = (1/4P_0^3)(24\Delta^2/P_0^2 + \Delta/\mu - 12c^2)$$

$$A_3 = (1/P_0^4)(3c^2 - 8\Delta^2/P_0^2 - \Delta/2\mu);$$

$$A_4 = -(1/4P_0^6)(4c^2 - 12\Delta^2/P_0^2 - \Delta/\mu)$$

For small p the energy spectrum has the form

$$\begin{aligned} \epsilon &= c(p - \gamma p^3 + \dots) \\ \gamma &= -A_2/2c^2 \end{aligned} \quad (59)$$

Y_{Ai}

Y_{iF}

$a_{\mathbf{p}+\mathbf{p}_1}^+ a_{\mathbf{p}} a_{\mathbf{p}_1}$	$a_{\mathbf{p}'}^+ a_{\mathbf{p}_1'}^+ a_{\mathbf{p}+\mathbf{p}_1}$
$a_{\mathbf{p}-\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}}$	$a_{\mathbf{p}_1'}^+ a_{\mathbf{p}_1} a_{\mathbf{p}-\mathbf{p}'}$
$a_{\mathbf{p}_1-\mathbf{p}_1'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}}$	$a_{\mathbf{p}_1'}^+ a_{\mathbf{p}-\mathbf{p}_1'} a_{\mathbf{p}_1}$
$a_{\mathbf{p}_1-\mathbf{p}_1'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_1}$	$a_{\mathbf{p}_1'}^+ a_{\mathbf{p}_1} a_{\mathbf{p}_1-\mathbf{p}_1'}$
$a_{\mathbf{p}_1'-\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}}$	$a_{\mathbf{p}_1'}^+ a_{\mathbf{p}_1} a_{\mathbf{p}_1-\mathbf{p}'}$
$a_{\mathbf{p}_1'-\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_1}$	$a_{\mathbf{p}_1'}^+ a_{\mathbf{p}_1} a_{\mathbf{p}_1-\mathbf{p}'}$

Equation 59 is then used to calculate the energy denominators in eq. 58

$$E_A - E_I = \epsilon(p) + \epsilon(p_1) - \epsilon(|\mathbf{p} + \mathbf{p}_1|), \text{ etc.}$$

We omit the details of the rest of the calculation and summarize the results. The viscosity coefficient is a sum of three parts

$$\eta = \eta_{\phi\phi} + \eta_{r\phi} + \eta_{rr}$$

representing the contributions from phonon-phonon, phonon-roton, and roton-roton scattering, respectively. The second of these is not calculated in detail in the L.K. theory because it is asserted to be negligible compared to η_{rr} at temperatures above 0.7°K., and negligible compared to $\eta_{\phi\phi}$ below 0.7°K. The other two

parts are called the phonon and roton viscosities. The phonon viscosity is estimated as

$$\begin{aligned}\eta_{\phi\phi} &= 8.7 \times 10^{-9} T^{-1/2} e^{\Delta/kT} \text{ poise, for } T > 1^\circ\text{K.} \\ &= 7.8 \times 10^{-10} (T^{1/2} e^{-\Delta/kT} + 4.8 \times 10^{-6} T^5)^{-1} \text{ poise, for} \\ &\quad T < 0.8^\circ\text{K.}\end{aligned}$$

Between 0.8°K. and 1.0°K. the phonon viscosity cannot be estimated accurately because processes involving a change in the total number of phonons interfere with the establishment of equilibrium in the phonon gas. While processes such as one phonon turning into two, or two into one, are forbidden, because it is impossible to satisfy both momentum and energy conservation, it is possible for two phonons to combine and produce three; the intermediate states II, III, IV, and V can be "real" states providing p' and p_1' have the particular values required by energy conservation. Many other terms in V_3 also can contribute to this process in second-order perturbation theory; Landau and Khalatnikov decided it was not worth while to calculate all these contributions since the process is important only in a very small temperature range. They claim that the relaxation time corresponding to such five-phonon processes can be estimated from experimental values for the coefficient of sound absorption, and conclude that at temperatures above 0.9°K. these processes take place more slowly than the scattering processes characterizing viscosity, whereas below 0.9°K. they are more rapid. It is only when phonon emission and scattering take place at about the same rate that Landau and Khalatnikov's method for solving the Boltzmann equation (by assuming rapid establishment of equilibrium in the phonon gas) becomes inapplicable.

It should be remarked at this point that while phonons obey Bose-Einstein statistics, they do not undergo a Bose-Einstein condensation because their total number is not fixed. Therefore the L.K. theory cannot explain the lambda transition without introducing some further hypotheses.

The roton viscosity cannot be estimated quantitatively from the theory because the nature of the interaction between rotors is unknown. Landau and Khalatnikov assume it has the form

$$V(r) = V_0 \delta(r)$$

where V_0 is a parameter to be determined empirically. They show that η_{rr} is independent of temperature for such a point interaction, and may be assigned a value $\eta_{rr} \approx 10^{-5}$ poise. This is about the value of the total viscosity of helium at 1.7°K. , where it is a minimum. The L.K. theory does not explain the subsequent increase in the viscosity as the temperature approaches the lambda point (2.2°K.).

Tisza (496) predicted that the viscosity would be proportional to the fraction of the "normal" component, which would have a gas-like viscosity proportional to

$T^{1/2}$; the viscosity of helium II would thus have a positive temperature coefficient, in disagreement with later experiments (23). The L.K. theory attributes the observed sharp increase in viscosity as the temperature is lowered below 1.7°K. to the strong temperature-dependence of the phonon-phonon scattering cross section.

We refer to the recent literature (109, 200a, 205, 216, 259, 260, 261, 262, 263, 309, 398, 404, 494, 549) for extensions and revisions of the L.K. theory. There also have been several discussions of the nature of phonons and rotors, and attempts to calculate equilibrium properties using various proposed wave functions for these excitations. Considerable work still needs to be done on the interaction of rotors with each other and with other excitations, and it is not clear whether roton scattering cross sections can be deduced directly from the postulates of quantum hydrodynamics without invoking atomic considerations. The L.K. theory, especially the rather messy calculations which we did not go into, needs to be put in a more presentable form before it can be regarded as an established scientific theory; up to now, Landau and his collaborators seem to have been more interested in getting quick results and suggestions for further experiments than in refining the original calculation of the shear viscosity coefficient. This is quite proper in such a rapidly developing field as low temperature physics, where a theoretical prediction can often motivate experimentalists to overcome many technical obstacles. However, we commend to the reader with a theoretical bent Lord Kelvin's remark, once again relevant after nearly a century (257):

A full mathematical investigation of the mutual action between two vortex rings of any given magnitudes and velocities, passing one another in any two lines, so directed that they never come nearer than a large multiple of the diameter of either, is a perfectly soluble mathematical problem; and the novelty of the circumstances contemplated presents difficulties of an exciting character. Its solution will become the foundation of the proposed new kinetic theory of gases.

The original vortex atom theory was, as Truesdell would say, "one of the many molecular speculations whose dry bones litter the by-paths of physics" (508). But a successful investigation of the interaction of two vortex rings, in their modern reincarnation as rotors, would be an important contribution toward the synthesis of quantum mechanics and hydrodynamics, and toward the construction of a theory which promises to achieve a consistent and unambiguous deduction of observable properties from postulates about collective molecular motions, without attempting the apparently hopeless task of describing the motions of all the individual particles. The possibility of constructing such theories is of considerable significance for both physics and chemistry.

Note Added in Proof

Since this article was written, there have appeared several papers deserving at least a brief mention. Davis, Rice, and Sengers (559) have derived by kinetic theory methods a formula which appears to be the generalization of Enskog's result (eq. 15) for the viscosity of dense fluids of hard spheres with "square-well" attractive forces. Sather and Dahler (576) also obtained formulas for the viscosity of dense fluids of "rough" spheres and of rigid convex molecular "cores" surrounded by "potential staircases." Livingston and Curtiss (566) modified the Enskog theory of dense fluids of hard spheres by attempting a more accurate determination of the non-equilibrium pair distribution function. Yih (583) analyzed the dual role of viscosity in the stability of the flow of rotating fluids. Fluctuation-dissipation expressions were used to calculate transport coefficients by Swenson (581) and by Nishimura and Mori (574). The other papers cited deal with entropy production due to viscous forces (563); derivation of the equations of hydrodynamics from statistical mechanics (571); the Landau-Khalatnikov theory (555, 584); turbulence (558); viscosity of glasses (554); non-Newtonian fluids (565); polymers (561); relaxation theory (569, 572); the superposition approximation (573); ultrasonic absorption (570, 578); empirical or semi-empirical formulas for viscosity (556, 564, 579, 580).

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IV. GLOSSARY OF SYMBOLS

Symbol and definition	Section where introduced
a_p Annihilation operator for phonons of momentum p	III-D
a_p^\dagger Creation operator for phonons of momentum p	III-D
b Volume occupied by spheres	III-A-1
c Velocity of sound	III-D
e Base of natural logarithms (2.718...)	I-D
f Distribution function	III-B
g Function used to define dimensionless relation between stress and deformation	II-B
h Planck's constant	III-C
\hbar $h/2\pi$	III-C
i, j Labels for molecules (1 to N)	III-B-1
i Label for intermediate state (I to VI)	III-D
i Imaginary unit $(-1)^{1/2}$	III-B-1
\mathbf{k} Wave number in Fourier expansion of the phonon field ($\mathbf{k} = p/h$)	III-D
k Boltzmann constant	I-D
m Mass of particle	I-A
n Set of occupation numbers for phonon states	III-D
n_p Number of phonons with momentum p	III-D
p Momentum of a phonon	III-D
p_i Momentum of molecule i	III-B-1
q_i Generalized coordinate (position or momentum)	III-B-1
q Point in phase space (set of all the q_i 's)	III-B-1

r	Rate of deformation	II-B
\mathbf{r}	Point in space (x, y, z)	III-B-2
s	Dummy time variable	III-B-2
t	Time	III-B
t_0	Characteristic time constant of a fluid	II-B
\mathbf{v}	Local hydrodynamic velocity	II-A
\bar{v}	Root-mean-square molecular velocity	I-A
y	Ratio of collision rate in dense gas to that in dilute gas	III-A-1
B	Equal to $-i(Lf_0)/f_0$ and also to $\beta S: \nabla \mathbf{v}$	III-B-2
E	Energy	III-B-2
\mathbf{F}_{ij}	Force between particles i and j	III-B-3
\mathbf{G}	Rate-of-deformation tensor, equal to $\nabla \mathbf{v}$	II-B
H	Hamiltonian operator	III-D
I, II, III	Invariant functions of the eigenvalues of the rate-of-deformation tensor	II-B
J	Momentum density	III-B-3
L	Liouville operator	III-B-1
P	Pressure tensor	II-A
P_0	Equilibrium hydrostatic pressure	II-A
S	Stress tensor	II-B
T	Temperature	I-D
V	Volume	III-A-1
V_{ij}	Potential energy of interaction between particles i and j	III-B-2
V_3, V_4	Terms in the phonon Hamiltonian operator containing 3 and 4 annihilation and/or creation operators, respectively	III-D
\mathbf{X}	External force	III-B-1
α	Operator function: $\alpha(x) = (e^x - 1)/x$	III-B-3
β	$1/kT$	III-B-2
γ	x, y component of rate-of-deformation tensor	II-B
δ	Dirac delta function	III-B-1
Δ	Minimum roton energy	III-D
ϵ	Energy of phonons	III-D
η	Shear viscosity coefficient	I-A
κ	Bulk viscosity = $\lambda + (2/3)\eta$	II-C
λ	Second viscosity coefficient	II-A
λ	Dummy variable in Mori's quantum-mechanical formula	III-C
μ	Roton "effective mass"	III-D
π	Ratio of circumference to diameter of circle (3.14...)	III-C
π	Momentum-current tensor	III-B-3
ρ	Density	I-A
ρ_0	Equilibrium average density	III-D
σ	Molecular diameter	I-A
τ	Plateau time	III-A-2
ψ	Wave function	III-D
ω	Phonon frequency ($\omega = cp/\hbar$)	III-D
∇	Differential operator ($\partial/\partial x, \partial/\partial y, \partial/\partial z$)	III-B-1
$\nabla_{r_i}, \nabla_{p_i}$	Same as ∇ with x replaced by r_{ix} or p_{ix} , etc.	III-B-1
1	Unit matrix	II-A

V. GUIDE TO THE LITERATURE

A number of review articles and books are available on various aspects of liquid viscosity; we begin with those on the statistical mechanical methods used in transport theory. The treatise by Hirschfelder, Curtiss and Bird (232) is now the standard reference for this subject, and it includes an account of Enskog's theory of dense gases and Eyring's rate theory of viscosity. Chapman and Cowling (88) give a more mathematical treatment of the classical kinetic theory of gases, and

of Enskog's theory of dense gases. Both are essential handbooks for research workers, but others may be discouraged by the large mass of material which apparently must be digested before one gets to the applications to liquid viscosity. The reader who wants to master the mathematical techniques used in the more recent theories, as opposed to the older kinetic theory methods, would be better advised to try Massignon's monograph (337). This exposition sets a high standard for clarity and simplicity yet does not sacrifice mathematical rigor.

Books on statistical mechanics (107, 135, 194) and irreversible thermodynamics (114, 115, 409) include applications of those disciplines to viscous flow problems. The books by Bingham (49), Brillouin (72), Dunstan and Thole (126), Hatschek (215), Merrington (346), Barr (30), Gemant (176) and Andrade (16) are entirely devoted to viscosity, and some of them devote a great deal of space to discussions of experimental methods and results, empirical formulas, and approximate theories and mechanisms. Bingham's book (49) contains a particularly comprehensive bibliography of work published before 1922; a later revision of this bibliography carried it up to 1931 (50).

There are many review articles which discuss particular theories of viscosity: by Graetz (188); Herzfeld and Smallwood, on Jäger's theory (223); Ferguson (147) and Barr (31) on the theories of Andrade and others; Burgers (84) on the theories of Andrade and van der Waals, Jr.; Jaeger (247) and Schulz (459) on the effect of chemical constitution on viscosity; Gemant (175) on the theories of Andrade, Eyring, Prandtl, Taylor and van der Waals, Jr.; a chapter in the book by Glasstone, Laidler, and Eyring (180) on Eyring's theory; Schubert (455) on German work during World War II; H. S. Green (194, 196) on the theory proposed by Born and himself; Harrap and Heymann (212) on the application of the Frenkel and Eyring theories to ionic liquids; Verschaffelt (524) on his own previous work; Rost (446) on the theories of Eyring, Andrade, Born and Green, and Vogel; Bondi (56) on the theories of Born and Green, Kirkwood, and Eyring; Collins (95) on the theories of Andrade, Born and Green, Collins and Raffel, Eyring, Kirkwood, and van der Waals, Jr.; Dow (120) on the pressure-variation of viscosity according to the theories of Frenkel, van Velden, Bondi, and Waring and Becher; Frank and Jost (161) on the application of theories of Enskog and others to the viscosity of liquid mixtures; Eyring (144) on his own theory and its application to Newtonian and non-Newtonian flow; Kochendorfer (281) on theories which explain viscous flow in terms of molecular rearrangements; Longuet-Higgins (324) on Kirkwood's and Enskog's theories; Cole (91, 92) on the work of Kirkwood and Eisenschitz; Eisenschitz (132, 133, 134, 135) on his own theory and those of Kirkwood and Born and Green. Some of the

most recent work on transport theory is discussed by Rice and Frisch (432) and by Mori, Oppenheim, and Ross (365); a good sample of original papers was presented at the Kirkwood Memorial Symposium (108) and published in November, 1960, issue of the *Journal of Chemical Physics*. Partington (397) gives an exhaustive survey of experimental methods, empirical and semi-empirical formulas, effects of temperature and pressure, relaxation theories, solutions of nonelectrolytes and of electrolytes, and good bibliographies on all these subjects. Dresden (120a) reviews quantum theories of transport phenomena.

Another group of articles is concerned with the molecular theory of the viscous flow of colloidal or high-polymeric systems (6, 144, 149, 160, 167, 170, 206, 220, 283, 300, 331, 335, 348, 368, 399, 442, 498, 550) and one of the supplements of the *Progress of Theoretical Physics* contains review articles on this subject (170). The books and articles on rheology mentioned below are also relevant.

The mathematical theory of Brownian motion, originally developed for the study of macromolecular or colloidal systems, also has been applied to monatomic liquids by Kirkwood (270), and the exposition of this theory by Chandrasekhar (87a) is helpful in understanding Kirkwood's theory. Cox (107) and Eisenschitz (135) have also discussed viscous forces from the viewpoint of Brownian motion theory. Lax (299) reviews theoretical work on fluctuations from the non-equilibrium steady state.

Since experiments on ultrasonic absorption often are interpreted as measurements of the bulk viscosity coefficient, we have included in the bibliography several publications on this subject, and on the molecular relaxation processes involved in ultrasonics (76a, 111, 137, 238, 279, 285, 333, 336, 437, 439, 448, 469, 490). The recent book by Herzfeld and Litovitz is particularly recommended (222). Bergmann's treatise (44) covers bulk viscosity as well as many other aspects of ultrasonics, and an appendix (45) brings his bibliography to a total of over 7000 items.

While viscosity is mentioned in almost every book on hydrodynamics, its effects are often largely ignored; we cite only those books which pay particular attention to the role of viscosity (53, 68, 105, 121, 145, 178, 183, 184, 208, 290, 297, 311, 339, 352, 353, 391, 392, 393, 394, 407, 414, 478, 487, 526, 528, 543). The early history of viscous hydrodynamics is discussed by Rouse and Ince (447) and by Truesdell (509, 510a) and others (227, 483). Boundary layer theory, which takes account of viscous effects only at fluid-solid interfaces, is the subject of books by Pai (392), Loitsianskii (321), Gortler (186), Schlichting (454), Brun (77), and Wick (539) and articles by Gadd (171), Geis (174), Howarth (236, 237), Kuethe (287), Rubesin (449), and Moore (360) (see also 105, 183, and 391). Turbulence theory is

reviewed in refs. 37, 38, 39, 105, 148, 173, 183, 209, 230, 307, 311, 312, 313, 393, 466, 503.

During the last few years, annual review articles have appeared in *Industrial and Engineering Chemistry* on "Molecular Transport Properties of Fluids" (254) and "Fluid Dynamics" (239, 386, 387, 388, 389, 390, 477); these provide useful surveys of current theoretical and experimental work.

Truesdell (506, 509) has reviewed the various attempts to provide rational generalizations of the classical linear theories of elastic and viscous substances, and has also recently (508, 513, 515) given non-technical accounts of some of this work. Reiner (422, 425, 426, 427), Bland (54), Gross (200), Tsui (517), and Coleman and Noll (93b) have also covered the more mathematical aspects of viscoelasticity theory. Books on rheology (73, 74, 89, 192, 213, 350, 428, 461, 462, 463, 465, 519) show how the observed properties of particular substances can be described by these theories. The British Rheologists' Club has published several volumes based on its conferences; the first of these (73) gives a good survey of the whole field, later volumes being collections of more technical papers (74, 350). The series of volumes edited by Eirich (129) contains many useful reviews of various aspects of rheology (see also 81, 347, 421, 458, 541, 545). Burgers and Scott Blair (85) and Treloar (504) have discussed rheological nomenclature.

Quantum-mechanical theories of viscosity usually have been developed with reference to liquid helium, and are thus covered in books and articles on low temperature physics and superfluidity (24, 25, 185, 190, 308, 322, 542). Many of the discussions are concerned with establishing the nature of the excitations involved—phonons, rotons, and quantized vortex lines—rather than with explicit calculation of the viscosity coefficient. Landau's theory of a Fermi liquid, intended to be applied to the isotope ^3He , is reviewed by Abrikosov and Khalatnikov (1), and the Landau-Khalatnikov theory of ^4He is reviewed by Khalatnikov (261, 262).

Touloukian (500, 502) has announced the establishment of a "Thermophysical Properties Research Center" for the collection and dissemination of data and information on seven physical properties, including viscosity, and the first volume of a *Retrieval Guide* has been published (501).

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