COMMENTS
ON THE EXPERIMENTAL AND THEORETICAL STUDY
OF TRANSPORT PHENOMENA IN SIMPLE LIQUIDS

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1. Introduction .................................................. 252
   References .................................................. 253

2. Comments on the Theory of Transport Phenomena ............. 254
   2.1. Some Simple Models .................................. 255
   2.2. Statistical Theories of Transport Phenomena .......... 259
   2.3. Formal Theories of Transport Phenomena ............. 276
   2.4. Phenomenological Analyses .......................... 289
   2.5. Transport Properties of Liquid Mixtures ............. 293
   2.6. Comments about More Complex Liquids ................. 314
   References .................................................. 317

3. Experimental Procedures and a Comparison between Theory and Observation ........................................... 320
   3.1. Experimental Methods .................................. 320
   3.2. Simple Liquids ........................................ 324
   3.3. Liquid Mixtures ....................................... 337
   3.4. “Complex” Liquids .................................... 352
   References .................................................. 359

4. Literature Survey ........................................... 360
   4.1. Bibliography of References ............................ 372
   4.2. Supplement (1966) ...................................... 399

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1. Introduction

This review is intended to survey the available experimental data relevant to transport phenomena in simple liquids and, wherever possible, to compare experiment with theory. For this reason, we have included an extensive survey of the literature as well as descriptions of both the experimental methods used to determine transport coefficients and the theories which may be used to calculate transport coefficients. Although it is necessary to discuss some very fundamental questions related to the nature of irreversibility in macroscopic assemblies of molecules, for the most part attention is focused on those theories that have been successfully reduced to the point that numerical predictions of the properties of a liquid may be made. For the details of all the theories tested the reader is referred to the original literature, but sufficient information is given about the physical assumptions inherent in each analysis to render intelligible the final formulas displayed herein.

The difficulties inherent in the construction of a molecular theory of liquids are widely heralded, but probably less widely understood. Provided that the conceptual structure of the theory is carefully defined and internally consistent, a dash of intuition can carry the theory a long way. At the present time, the theory of the equilibrium properties of a liquid* is in quantitative agreement with experiment at densities up to one-third to one-half of the normal liquid density. At higher densities the theory is qualitatively correct, but the quantitative discrepancies become large (\(~25\%\), say for Ar at \(T = 84^\circ K\), \(p = 1\ atm\), when one compares the theoretical and experimental pressures, internal energies, etc.). For certain limiting cases, e.g., the rigid sphere fluid, theory and experiment (in this case the experiment is a computer calculation) are in essentially quantitative agreement over the entire fluid domain. Of course, the available theories of critical phenomena and phase transitions are badly inadequate, and in these cases there are qualitative differences between theory and observation.

In the preceding paragraph we hinted that a moderately satisfactory theory of liquids can be developed with the aid of intuitive constructs. We use the words “moderately satisfactory” to indicate that a complete theory should, in principle, involve only well-defined mathematical manipulations based on transformation of the exact equations of motion, phase integral, etc. To the extent that intuitive constructs bypass mathematical difficulties, and then can later be shown to represent certain well-defined mathematical operations or approximations, a

* See, for example, Hirschfelder, Curtiss, and Bird [4] and Rice and Gray [11].
theory with intuitive content can be, more or less, transformed into a "rigorous" theory. Without further apology, we shall therefore adopt the attitude that the experimental test of theoretical predictions is a valid procedure for discriminating among possible intuitive arguments, mathematical approximations, etc., even when it is, from the point of view of pure logic, inherently impossible to give a completely unambiguous answer to the question: Which is correct?

There have been many different attempts to construct theories of transport phenomena.* Of these, the activated state theory [2], the corresponding states theory, the statistical mechanical theory leading to kinetic equations [10, 11], the autocorrelation function theory [6, 8], and the theory of mixtures are reviewed in Section 2. Section 3 is devoted to a survey of the principles underlying the most important of the experimental methods used to determine transport coefficients, and to an examination of the experimental data. In Section 3 we attempt to define the accuracy to which the several theories describe the data, to interpret the deviations between experiment and theory, and to suggest the directions in which new experimental and theoretical work would be most valuable. The remaining section of this chapter includes a tabular display of bibliographical information and an extensive bibliography of the relevant literature.

REFERENCES

General Bibliography of Theories of Transport Phenomena:


* A comprehensive, but not exhaustive, bibliography is given at the end of this section.
2. Comments on the Theory of Transport Phenomena

The starting point for the discussion of transport phenomena is the description of the macroscopic dissipative processes in terms of the constraints which define the nonequilibrium state of the system, and a set of coefficients which measure the rates of dissipation. Dissipative processes arise from the transport of mass, momentum, and energy. In each case there exists a phenomenological relationship between a flux and the force which is responsible for the flux. In the cases of energy and mass transport we have the Fourier and Fick equations,

\[
\begin{align*}
\mathbf{q} &= \kappa \nabla T \\
\frac{\partial T}{\partial t} &= \kappa \nabla^2 T \\
\mathbf{J}_m &= D \nabla c \\
\frac{\partial c}{\partial t} &= D \nabla^2 c
\end{align*}
\]

(1)

with \(\mathbf{q}\) and \(\mathbf{J}_m\) the energy and mass fluxes, \(\kappa\) and \(D\) the coefficients of thermal conductivity and diffusion, \(T\) the temperature, and \(c\) the concentration of one of the two components in the medium wherein diffusion is occurring. In the case of momentum transport the stress tensor \(\sigma\) and the rate of strain \(\dot{\varepsilon}\) play primary roles. For a Newtonian fluid the principal shearing stresses are proportional to the corresponding rates of strain and

\[
\sigma = [-p + (\phi - \frac{2}{3} \eta) \mathbf{1} + 2\eta \dot{\varepsilon}] \mathbf{1}
\]

(2)

with \(\phi\) and \(\eta\) the coefficients of dilatational and shear viscosity, \(\mathbf{u}\) the fluid velocity, \(p\) the pressure, and \(\mathbf{1}\) the unit tensor. The stress law (2) when introduced in the equation of motion of the fluid leads to the Navier-Stokes equation—the starting point for the study of fluid dynamics.

For the simple fluids considered in this book, Eqs. (1) and (2) provide an accurate representation of dissipative behavior. The coefficients \(\kappa, D, \eta, \) and \(\phi\) may be determined experimentally by a variety of methods based upon suitable solution of the appropriate differential equation (see Section 3). It is found that all of the transport coefficients vary when the temperature and density of the liquid are varied. It is observed
that at constant external pressure $D$ increases exponentially and $\eta$ decreases exponentially as $T$ is increased. Under the same conditions $\kappa$ is much less sensitive to changes in temperature than are $\eta$ and $D$. For most simple liquids $D$ is of the order of $10^{-5}$ cm$^2$/sec, $\kappa$ of the order of $10^{-4}$ cal/cm sec$^\circ$C, and $\eta$ of the order of $5 \times 10^{-3}$ dyne sec/cm$^2$. For liquids with extensive hydrogen bonding, such as polyhydric alcohols, $\eta$ may be very much larger, as it also is for long chain molecules in general. The dilatational viscosity $\phi$ is partially responsible for the attenuation of sound in a liquid. In the case of liquid Ar, the only simple system studied to date, $\phi$ is of the same order of magnitude as $\eta$ ($\phi/\eta = 1.4$). For complex liquids, such as polyhydric alcohols, $\phi$ can be related to the relaxation of the internal motions of the molecules in the liquid, and can be very large in magnitude.

Suppose that, for some liquid, the several transport coefficients have been determined as a function of temperature and density. How can these data be interpreted in terms of molecular dynamics and the structure of the liquid? The extant theories of transport phenomena, which deal with just such an analysis, may be conveniently grouped into four classes: (a) simple quasi-solid or quasi-gas models with many empirical parameters, (b) phenomenological analyses based upon the principle of corresponding states, (c) statistical mechanical theories starting from the rigorous Liouville equation but employing simplifying approximations, and (d) developments which lead to formally exact results, but which may be difficult to use for a practical calculation. In the following we examine each of these classes in detail. Mathematical details of the derivations are available in the literature and will not be repeated herein. Indeed, we shall focus attention exclusively on the nature of the physical arguments, the validity of the approximations, and the implications of the theory in other contexts. In a later section we shall also examine in detail the agreement between theory and experiment.

2.1. SOME SIMPLE MODELS

Perhaps the simplest of all descriptions of the liquid state are based on the use of quasi-crystalline model geometries. In the equilibrium theories it is usually supposed that the volume occupied by the liquid may be spanned by a virtual lattice, thereby subdividing the volume into cells. In some analyses only a single molecule can occupy a cell while in others multiple occupancy and/or zero occupancy ("holes") are included in the description. In all cases, however, the phase space available to the molecules is severely restricted by the geometric constraints expressed in terms of cell occupancy. Using the perfect lattice as the unperturbed
reference system is, superficially, an attractive suggestion. Indeed, in the case of the equilibrium theory, it may be shown that if the analysis is carried to all orders of perturbation theory, then there is obtained an exact evaluation of the canonical partition function. However, it has not proven possible to go beyond the lowest order terms in the expansion, and these provide a disappointingly poor approximation for the equilibrium properties of liquids. Are there, then, any uses for quasi-crystalline models of the liquid state? No completely unambiguous answer can be given to this question. In the case of equilibrium properties, quasi-crystalline models of local liquid structure may sometimes be used to advantage in the interpretation of the radial distribution function $g^{(2)}(R)$. While it is recognized that long range crystalline order is absent in the liquid, the local arrangement of the neighbors of each molecule is regarded as a blurred replica of the first several coordination shells of a single crystal lattice or of a superposition of several lattice types. The number of neighbors in each diffuse coordination shell is estimated as $\int 4\pi R^2 \rho g^{(2)}(R) \, dR$ under the corresponding peak of the radial distribution function, where $\rho$ is the bulk density of the liquid. In this way it is inferred that, for example, the local structure of liquid mercury corresponds to an approximately close-packed array of spheres. For the case of water, the liquid is regarded as a three-dimensional net in which each water molecule is linked to four neighbours by hydrogen bonds. By superposing coordination structures of the $\beta$-quartz, trydymite, and close-packed types, a synthetic $g^{(2)}(R)$ may be constructed which is in substantial agreement with experiment. At low temperatures the $\beta$-quartz structure predominates, and at high temperatures the contribution of the close-packed structure increases.

In a similar manner the structure of liquid hydrocarbons is represented as approximating the arrangement realized in the axial close packing of slender rods. The x-ray scattering curves of aliphatic alcohols exhibit inner peaks not observed for the corresponding hydrocarbons. This peak may be qualitatively interpreted if it is assumed that the alcohol molecules are linked in chains by hydrogen bonds between the hydroxyl groups while the aliphatic groups remain approximately close packed as in the corresponding hydrocarbons.

The quasi-crystalline interpretation of the liquid pair correlation function can also be used to advantage in discussing the dielectric constant. When neighboring molecules are strongly correlated, as for example by the presence of a hydrogen bond, it can be shown that

$$
\epsilon'(0) - n^2 = \frac{3\epsilon'(0)}{2\epsilon'(0) + n^2} \cdot \frac{4\pi N}{3kT} \mu^2 (1 + z\langle \cos \gamma \rangle)
$$

(3)
with \( n \) the refractive index and where \( \langle \cos \gamma \rangle \) is the average of the cosine of the angle between neighboring dipoles with electric moment \( \mu \), and there are \( z \) nearest neighbors to any dipole. Kirkwood has calculated \( \varepsilon'(0) = 63 \) for water at 300°K, whereas the observed value is 78. The predicted temperature dependence of \( \varepsilon'(0) \) is also in fair agreement with observation. Similar agreement between theory and experiment is obtained when other hydrogen bonded liquids, such as the alcohols, are considered [1].

In general, quasi-crystalline models of a liquid are of most use when the correlation between molecules is very strong because of the presence of a specific orientation dependent interaction such as a hydrogen bond. For simple monatomic fluids, quasi-crystalline models are far less useful and often lead to erroneous predictions because of their inherent overestimate of the molecular ordering. For monatomic fluids, \( g^{(2)}(R) \) computed from a quasi-crystalline model has oscillations above and below the asymptotic value of unity as much as ten molecular diameters from an arbitrary molecule, whereas the observed \( g^{(2)}(R) \) has reached unity after only three or four molecular diameters.

In the description of transport processes the role of the quasi-lattice is more important, since the local geometry of the liquid influences the flow of mass, momentum, and energy. Consider the model used to describe diffusion. It is assumed that, in order to move, a molecule must be close to a vacant site (cell) from which it is separated by a free energy barrier. The flux of matter then depends on the rate of surmounting the barrier and the concentration of vacancies. In the case of the shear viscosity, the effect of the relative motion of two planes of atoms on the frequency of atomic jumps over the barrier is used to relate the flow of momentum with the shear strain. The reader should note that in each case it is assumed that the basic step requires thermal activation, i.e., that an intermediate geometric configuration midway between the initial and final molecular structures exists, and that the ratio of the concentration of such activated states to the concentration of initial states is determined by \( \exp(-\Delta G^*/RT) \) with \( \Delta G^* \) the free energy of activation. This theory predicts that \( D \) and \( \eta \) vary exponentially with temperature, as is observed. The quasi-crystalline theories do not relate the parameters required to calculate \( D, \kappa, \) and \( \eta \) to the intermolecular potential or to \( g^{(2)}(R) \) and therefore are really parametric representations rather than molecular theories. Moreover, they cannot account for the temperature dependence of \( D \) and \( \eta \) if the density is maintained constant rather than the pressure.

One fundamental problem raised by this representation is immediately apparent. The energy acquired by a "jumping" molecule in order that
it may pass over the free energy barrier must be dissipated in a time short relative to the passage time. If this is not true, there is a large probability that the "hot" molecule will return to its original position, and irreversibility will depend on a bias in the end points of a many-jump process. In contrast, if the "hot" molecule loses energy rapidly, then only one jump takes place and an irreversible flow is generated because any succeeding jump is uncorrelated with the jump just completed.

This picture implies the existence of a mechanism characterized by two different length scales in the free path distribution, as pointed out by Alder and Einwohner [2]: One length corresponds to the particle rattling in its cage, and the other one has the magnitude of the intermolecular distance. Therefore the path distribution should exhibit two peaks, a conclusion which is in contradiction with the Alder and Einwohner "computer experiment" for hard spheres; i.e., the observed fluid free path distribution decays monotonically nearly as an exponential. Furthermore, the probability of free paths of a length larger than the molecular distance is seen to be less (by many orders of magnitude) than that required by the Eyring theory to predict the diffusion coefficient.

A better picture of motion in a liquid is provided by a model proposed by Cohen and Turnbull [3]. In this model a molecule can only move if a void of critical size \( V^* \) opens up adjacent to the molecule. It is supposed that such voids can occur by the occasional random coalescence of the free volume of the liquid. If \( \sigma \) is the diameter of a molecule, Cohen and Turnbull show that

\[
D = \left(\frac{\sigma}{6}\right)\left(\frac{3kT}{m}\right)^{1/2} \exp\left(-\frac{\gamma V^*}{V_f}\right)
\]

where \( \gamma \) is a numerical constant and \( m \) is the mass of the molecule. This equation qualitatively accounts for the behavior of complex molecules and provides an interpretation of the fluid behavior in the glass region where the simple form of the activated state model fails. Equation (4) does not, however, accurately describe the behavior of simple fluids. For the case of simple molecules the intermolecular repulsive potential rises much less steeply (on a scale in which the molecular diameter is the unit of length) than does the intermolecular repulsive potential of complex molecules, and this difference is one source of the errors inherent in (4).

As already hinted, of greater importance than any of the criticisms made thus far is the complete omission in the models mentioned of any attempt to understand the origin of irreversibility. Although in the theory of self-diffusion in a crystalline medium it can be shown that the jumping atom indeed does lose energy through coupling with the
surrounding lattice, no quasi-crystalline model of the liquid state includes an analysis of energy dissipation in this sense. Moreover, the complicated many-body dynamical problem which must be analyzed (in a crystal the existence of a normal mode spectrum enables this problem to be solved with satisfactory accuracy), when coupled with the formally inconsistent coupling of kinetic and statistical concepts, makes it unlikely that a logically satisfactory theory of transport in liquids can be based on the use of quasi-crystalline models. It is not a simple matter to convert the time reversible equations of motion for the molecules to a form which will yield the time irreversible fluxes (1). We shall discuss this matter in detail later. For the present we merely note that dissipative processes can be described in terms of a dynamical event, possibly complex, which is independent of prior dynamical events. Careful consideration must be given to the nature of the molecular correlations, the relevant time scales in dissipation, and the role of perturbing forces [4].

2.2. Statistical Theories of Transport Phenomena

The development of a statistical theory of transport phenomena in liquids requires consideration of many problems, among which are:

(a) analysis of the means by which the time reversible equations of classical and quantum mechanics that are used to describe the motions of molecules lead to the time irreversible flux equations displayed in Eq. (1);

(b) derivation of a suitable kinetic equation determining the time evolution and phase dependence of some ensemble probability distribution; and

(c) solution of the kinetic equation to obtain relationships between the macroscopic parameters $\eta$, $\phi$, $\kappa$, and $D$ and the intermolecular potential, number density, temperature, etc.

The reader should recognize that the calculation of transport coefficients is, in fact, only a small part of the general problem of describing time-dependent phenomena. Namely, it is concerned with that state of a fluid in which all time dependence resides in the local hydrodynamic flow velocity. The general problem also involves the description of those short-lived processes whose time dependence is explicit. Such processes are generally non-Markovian of a high order, and the asymptotic approach of the exact kinetic equations describing them to the Markovian equations of the hydrodynamic regime with which we are concerned in this section is discussed in Section 2.3.
As we shall see, the exact kinetic equations for a dense fluid can be displayed only in the most formal way at the present time. Consequently, their asymptotic Markovian form is unknown, and the forms of the equations derived to describe a dense fluid are based on an intuitive analysis of the nature of random processes. Indeed, at present the only kinetic equations applicable to the description of phenomena in the liquid state are those derived using the time-smoothing technique introduced by Kirkwood [5], or its equivalent.

The method of obtaining equations satisfied by the one- and two-molecule distribution functions $f^{(1)}(\Gamma_1; t)$, $f^{(2)}(\Gamma_2; t)$, respectively, is essentially that of integrating the $N$-molecule distribution function $f^{(N)}(\Gamma_N; t)$ over the subphase space of all the other molecules in the system. Now, $f^{(N)}$ satisfies the Liouville equation, and is not known explicitly. Therefore, one may only obtain differential equations for $f^{(1)}$ and $f^{(2)}$ by integrating the Liouville equation term by term. The result is a coupled hierarchy of equations; i.e., the equation for $f^{(1)}$ also involves $f^{(2)}$, the equation for $f^{(2)}$ also involves $f^{(3)}$, and so on. It is necessary to truncate this hierarchy at some point in order to obtain closed equations for $f^{(1)}$ and $f^{(2)}$.

For a classical fluid we describe the system of $N$-structureless molecules in the volume $V$ by use of the Hamiltonian equations of motion. These equations have some interesting general implications. Since there is one equation for each degree of freedom of the system, it follows that the phase of the system at any instant is uniquely determined by the phase at any other instant. In accordance with the definition of a Markovian random process, it follows that the phase of the system $\Gamma_N$ may be regarded as a Markovian process of a simple kind. (The transition probability is a $\delta$-function, since the increment of the variable $\Gamma_N$ has only one possible value for each time instant.) The kinetic equations for the reduced distribution functions $f^{(1)}, f^{(2)}, \ldots$, are concerned with the random variables $\Gamma_1(1), \Gamma_2(1, 2), \ldots$, which are of smaller dimensionality. Now, it is well known that the projection of a Markovian process of $6N$ dimensions onto a space of smaller dimensionality ($6, 12, \ldots$, dimensions) generally yields a random process of higher order. Thus, $\Gamma_1(1), \Gamma_2(1, 2), \ldots$, will be non-Markovian processes of high order. This general feature has been obtained in the analysis of Prigogine and co-workers. They find that the stochastic interaction term has the form of a time convolution over the history of the variable. The important result is that when the system has reached a stationary state, the kinetic equations reduce to Markovian form.

At this point it is legitimate to raise the question: What is the connection, if any, between the equations of hydrodynamics in microscopic or
macroscopic form and stationary states? The first answer is obvious: It is quite possible to discuss the hydrodynamics of a system in a nonequilibrium stationary state in which transport coefficients play a crucial role. This is a rather trivial statement, and the argument may be developed much further. The equations of hydrodynamics deal adequately with processes which are nonstationary on a macroscopic time scale. Useful results have been obtained even for such rapidly varying processes as shock waves in dilute gases. All these processes are, in fact, very slow compared to the time scale of molecular fluctuations, on which non-Markovian processes are important. Generally, one would expect that the kinetic equations should be Markovian if the processes described are sufficiently slow that local thermodynamic equilibrium is maintained in the fluid.

The problem of truncating the coupled hierarchy of kinetic equations has, therefore, two distinct features. Since an integration over the subphase space of \((N - 1)\) or \((N - 2)\) molecules leaves the equations completely reversible, the truncation procedure must in the first place make the equations irreversible. Second, it must provide a means of singling out the Markovian features that the kinetic equations contain in the hydrodynamic regime. The introduction of irreversibility is not difficult; it is merely contingent upon the particular method by which the Markovian feature of the truncation is achieved. At the present time, however, no systematic procedure for obtaining the Markovian feature is known, and the one we adopt is based on that first proposed by Kirkwood [5].

Consider now the relationship between non-Markovian processes in the subphase spaces of one, two, ..., molecules, and the ultimate transition to a Markovian kinetic equation defined on these same subphase spaces. We wish to assert that an \(n\)th order process can be treated as an \(n\)-dimensional Markovian process, the reduction being accomplished by grouping the states of the process into hyperstates. Each hyperstate in the Markovian process contains information about the history of the system during the interval \(t_m\) to \(t_{m+n-1}\). Much of this information is superfluous for the evaluation of the distribution functions in the hydrodynamic regime, but the information needed is contained within the hyperstate. The method of truncation of the hierarchy of coupled equations for the distribution functions is, therefore, a means of extracting the relevant information from the hyperstate. The particular contribution to the theory made by Kirkwood, which we have already mentioned, is the hypothesis that the relevant information for present purposes is contained in the exact distribution function averaged over an interval of time \(\tau\). The average value for an interval \(\tau\) on the fine-grained time
scale is then associated with a single point on a coarse-grained time scale, and the process is known as coarse graining (in time*). The kinetic equations obtained in this way are, in principle, difference equations, but it turns out that the times during which changes become significant on a hydrodynamic scale are so long compared to the coarse-graining time that no significant error is introduced by treating the differences as differentials.

The introduction of irreversibility which must accompany the coarse graining is accomplished by the assumption that a time interval \( \tau \) exists such that the dynamical behavior of the system during one interval is related in a simple statistical manner to the dynamical events of the previous interval. It may be shown that the statistical character of the relation is sufficient to render the process irreversible.

The statistical assumption, or \textit{ansatz}, can be analyzed on the basis of an intuitive picture of the dynamics of liquid molecules. Consider first the Fokker-Planck equation describing the behavior of a Brownian particle. This equation describes a stochastic process under conditions such that the transition probability (for the phase \( \Gamma \) of the Brownian particle) is that for a stationary Markovian process. In turn, this may be shown to be the result of allowing the time resolution of the description of the Brownian particle to be sufficiently coarse that transient behavior associated with the approach to local equilibrium in the molecular motions cannot be resolved. Thus, the description of Brownian motion as a Markovian process applies only to the discussion of processes taking place on a time scale longer than some \( \tau_c \) characteristic of the liquid molecules. In the development of the theory \( \tau_c \) is chosen using physical criteria such that the basic dynamical event (in this case molecular fluctuations) is statistically independent of prior events. Were this not the case, the transition probability connecting two dynamical states of the Brownian particle would not be Markovian.

The problem of Brownian motion is concerned with numerous small momentum transfers, or numerous small particle displacements. At the other extreme of behavior, where momentum transfers may frequently be large and where displacements may be large, is the dilute gas. Transport phenomena in a dilute gas are usually described by a one molecule distribution function which satisfies a kinetic equation (Boltzmann equation) in which the effects of molecular interaction appear in the form of isolated binary collisions. The rate of change of the distribution function is determined by the slow secular variations of \( f^{(1)} \) due to streaming in phase space on which are superimposed the effects

* It is possible also to coarse grain in space; similar kinetic equations are obtained.
of the binary collisions. On the average, a molecule moves a long distance (relative to its size or the range of the intermolecular forces) before undergoing an encounter. Although there is a large volume of phase space wherein there occur small angle deflections resulting from binary collisions, large angle deflections are also frequent. Indeed, large angle deflections are responsible for most of the transport of energy and momentum due to collisions.

There have been numerous attempts to derive the Boltzmann equation from the first principles of statistical mechanics with the aid of some auxiliary nonmechanical assumptions that relate to the irreversibility [5-16]. The assumptions required to effect a derivation are basically three in number: the truncation of interactions of higher order than binary collisions, the condition of molecular chaos (i.e., the condition that every pair of colliding molecules is statistically independent prior to the collision), and the slow secular variation of \( f^{(1)} \) in space. Of these conditions, only the molecular chaos is responsible for the irreversibility.

The restriction that the singlet distribution function vary slowly in space is very mild. Even under the extreme conditions in a shock front it may be a useful approximation, and under ordinary circumstances it is certainly valid to the same extent that local parameters such as temperature, pressure, etc., can be employed as useful variables. The binary collision approximation is also valid in the limit of low densities, and we therefore focus attention on the question of molecular chaos and the related coarse graining.

At least part of the difficulty in analyzing the chaos property arises from the intuitive nature of this assumption. That is, the usual mental image of the gaseous collision process leads to the expectation that chaos (lack of correlation in both positions and momenta) will be produced even if absent initially, though this may require many collisions to accomplish. However, if such chaos requires a time interval corresponding to many collision times, then it does not lead to the Boltzmann equation which describes transport phenomena in the dilute gas. For in the Boltzmann equation the binary collisions are taken to be independent, and the relevant time interval is therefore long compared to the duration of a collision but short compared to the mean time between collisions. The problem separates into two overlapping questions: Is the initial distribution "chaotic" and is the chaos propagated?

Consider first the question of initial chaos. Grad has claimed that the class of functions \( \{ f^{(2)} \} \) which is obtained by integration of the class

* The successive collisions suffered by a particular molecule are the result of its motion through an environment which is assumed to be (statistically) unaffected by the rebounding molecules.
\( f^{(n)} \) chosen to be consistent with a given singlet function \( f^{(1)} \) converges to the product \( f^{(1)}(1)f^{(1)}(2) \) as \( n \to \infty \). The argument centers on the symmetry of the distribution function in the arguments, positions, and momenta, with the net result that the probability density is peaked in those regions of phase space for which the factorized product condition is valid. However, it is not clear that this theorem is of any use for the study of dense media, since those portions of phase space where chaos is not exhibited are just the regions most important for the description of the liquid phase. In the case of the dilute gas, where at equilibrium the pair correlation function is unity, the demonstration that the pair distribution approaches a product of singlet distributions is tantamount to the demonstration that chaos exists. Note that so far we have said nothing about the temporal or spatial scale over which chaos is to be expected. To examine this question we assume that at a given time chaos is established. It is clear that whether chaos will or will not be propagated depends in part on the time scale for which the Liouville equation is solved. Even with an initially factorized distribution, it is certainly true that for time intervals that are short compared to the mean time between collisions, a pair of molecules that has just collided will be strongly correlated with one another. It is only by the intercession of further collisions with third and fourth molecules that this correlation can be destroyed. Whereas at equilibrium, \( g^{(2)} \) has a correlation range (i.e., a volume element within which it differs from unity) only of order of magnitude of the range of intermolecular forces, out of equilibrium the correlation range may be much larger. This is a result of the persistence of the initial state. Briefly stated, as time increases there will be an increasingly large number of initial configurations that result in collision, and thus in a certain sense the correlations grow in time. In the absence of intervening collisions the correlations for a pair of molecules are essentially constant over a distance equal to the relative velocity multiplied by the time. Now, the derivation of the Boltzmann equation by Kirkwood \[5\] uses coarse graining to isolate a binary collision and define the extent of the memory of correlation. That is, the fundamental dynamical event is taken to be a binary collision and it is assumed that \( \tau \) is long compared to the duration of a collision but short compared with the time between collisions. A second coarse graining is later performed upon the integrand of the collision operator. We immediately note that the formal effect of coarse graining is to limit the correlation time to \( \tau \), successive intervals of length being uncorrelated. If \( \tau \) is taken as long relative to the duration of an encounter, but short relative to the time between encounters, then coarse graining over an interval successfully breaks the correlations between successive collisions. This truncation is
accomplished by taking the length of the collision cylinder defining the volume of space relevant to two molecules about to collide as proportional to $\tau$. There remains, however, an indirect correlation due to the coupling through third molecules. Consider the following collision sequences: molecule 1 collides with molecule 2, molecule 2 rebounds and collides with molecule 3, etc., the trajectories being so constructed that molecules 2 and 3 would not have collided at the time, except for the prior collision with molecule 1. It is clear that for this example molecule 1 has influenced the collision between molecules 2 and 3. For geometric reasons, the correlation due to these indirect collision sequences must decrease with increasing distance between molecules 1 and 2. That is, in a homogeneous gas, the probability that no intermediate collisions occur between the indirectly coupled collision of molecules 2 and 3 following the collision of molecules 1 and 2 is of the approximate form $\exp(-R_{12}/\lambda_I)$, where $\lambda_I$ is the mean free path and $R_{12}$ is the distance between molecules 1 and 2. Therefore, outside a sufficiently large volume element in configuration space, the correlation due to indirect collision paths vanishes. We may now state a more restrictive condition on the time interval used for the second coarse graining. It must be chosen so as to render the correlations due to indirect collisions negligible. Note that a time interval is equivalent to a linear extension of order $\Delta R(\tau)$. Clearly, in the dilute gas, $\Delta R(\tau)$ ought to be longer than the range of the intermolecular potential but shorter than a mean free path.

The case of a dense fluid is qualitatively different. The meaning of molecular chaos in a dilute gas is that molecule 2 (which is due to collide with molecule 1) has approached molecule 1 from infinity and its distribution of possible velocities has not been affected by collisions with molecules which have recently collided with molecule 1. In a dense fluid, molecule 1 may undergo a rigid core, i.e., strongly repulsive, collision with a second molecule which has for some time past been in the region of the first coordination shell of molecule 1. Thus, molecule 2 should have an intimate statistical “knowledge” of molecule 1, and may indeed have undergone a rigid core collision with molecule 1 in the immediate past. However, if the quasi-Brownian motion produced in the molecules by the van der Waals part of the forces is sufficiently effective in causing molecule 2 to forget its previous experience, then successive rigid core collisions should satisfy the simple form of molecular chaos used.

But aside from questions of how chaos and time coarse graining are related in very short time intervals, it is pertinent to inquire how much chaos is required for the derivation of the Boltzmann equation, and whether or not chaos propagates when large time intervals are considered.
It has not yet been possible to prove in general that chaos is propagated by the Boltzmann equation although it can be shown to be true for some configurations. These configurations are just those for which the pair of molecules is widely separated and do not collide. The basic idea is that when the molecules are not close to one another, \( f^{(2)} \) and \( f^{(1)} f^{(2)} \) have similar time dependence. The residual difference, \( f^{(2)} - f^{(1)} f^{(1)}(2) \), can then be related to the residual differences between products of singlet distribution functions and the corresponding higher distribution functions, \( f^{(n)} \). When the molecules do not collide, simple rectilinear trajectories are traversed, and thereby the two molecule residuals are related to the initial values of the \( n \)-particle residuals. But if \( f^{(n)} \) is initially chaotic, the \( n \)th order residuals tend to zero and the time dependence of the two molecule residuals also tends to zero. Thus, the initial chaos is propagated in that set of configurations in which collisions do not occur. Due to the large correlations in the short time immediately following a collision, no general proof of the propagation of chaos has yet been constructed.

To complete this discussion of coarse graining we seek a consistency condition on the passage from the non-Markovian to the Markovian description of the fluid. In a sense, the distribution function may be thought of as a vector in a continuous space whose components represent the occupation probabilities of the various states of the phase space. In the most general case, the probability of finding the set of states \( (p^{(n)}, \{n\}) \) depends on the past history of the system. There are, however, two limiting cases where the past can be ignored [18]:

(a) If the probability for moving to the set of states denoted \( (p^{(n)}, \{n\})_t \) at time \( t \) from any substate \( (p_i, i)_{t-\tau} \) at time \( t - \tau \) is the same for all the states of \( (p^{(n)}, \{n\})_{t-\tau} \), then the probabilities for being in each substate of \( (p^{(n)}, \{n\})_{t-\tau} \) do not affect the outcome of the transition \( (p^{(n)}, \{n\})_{t-\tau} \rightarrow (p^{(n)}, \{n\})_t \).

(b) If, no matter what the sequence \( (p^{(n)}, \{n\})_t, (p^{(n)}, \{n\})_{t-\tau}, \ldots \), is, we always end up with the same assignment of probabilities for being in each of the states in \( (p^{(n)}, \{n\})_t \), then the preceding sequence can have no influence on the transition \( (p^{(n)}, \{n\})_{t-\tau} \rightarrow (p^{(n)}, \{n\})_t \).

These conditions are used as follows: Let it be assumed that there exists a time interval \( \tau \) such that the following dynamical event, defined in \( \tau \), defines a Markovian process. The dynamical event consists of a strongly repulsive binary encounter followed by a quasi-Brownian motion of the pair of molecules in the fluctuating field of all the neighboring molecules. Because the destruction of correlations by the quasi-Brownian motion is efficient, successive strongly repulsive encounters are
TRANSPORT PHENOMENA IN SIMPLE LIQUIDS 267

Consider now the relationship between this hypothesis and the consistency conditions imposed by coarse graining. Which of the two limiting cases is applicable in our situation? Consider the description of the strongly repulsive binary encounter portion of the fundamental dynamical event. The transition probability for scattering from the pair of momentum states $\mathbf{p}_1^*, \mathbf{p}_2^*$ to $\mathbf{p}_1, \mathbf{p}_2$ is a function of the impact parameter, intermolecular potential, etc. Clearly, the scattering to a set of final states $\mathbf{p}_1, \mathbf{p}_2$ is not independent of $\mathbf{p}_1^*, \mathbf{p}_2^*$ and, therefore, limiting case (a) is inapplicable. If coarse graining is to perform the function required we must establish that condition (b) is applicable.

If, no matter what the sequence $(\mathbf{p}^{(n)}, \{n\})_1, (\mathbf{p}^{(n)}, \{n\})_2, \ldots$, is, we always end up with the same assignment of probabilities for being in each of the states of $(\mathbf{p}^{(n)}, \{n\})$, then it is necessary that the relaxation time for return to the states of $(\mathbf{p}^{(n)}, \{n\})$ be short relative to the time interval on which the fundamental dynamical event is defined. Thus, if it can be shown that the relaxation time for the return to local equilibrium is much shorter than the time between strongly repulsive binary encounters, then the initiation of the dynamical event consisting of a strongly repulsive binary encounter followed by a quasi-Brownian motion always starts from the same distribution function. In this case the probabilities for being in each of the states of $(\mathbf{p}^{(n)}, \{n\})$, just define the distribution function, and the conditions of case (b) are satisfied.

A very interesting and fundamental analysis of the role of coherence time in the statistical mechanics of irreversible processes has been given by Fano [18b], using some ideas and techniques introduced by Zwanzig [18c]. Fano shows that in the limit that the dynamical coherence between a subsystem and its surroundings (reservoir) is short lived, the effective interaction between reservoir and system is weak irrespective of the magnitude of the intermolecular potential. From Fano's analysis, Hurt and Rice have developed a formal coherence time expansion for the classical fluid, and show that [19]:

(a) In the limit of short memory of dynamical coherence, the Rice-Allnatt kinetic equations (see following) are a valid description of steady state phenomena in the liquid.

* Recent studies of neutron diffraction from liquid Ar confirm the accuracy of this hypothesis (Dasamacharya and Rao [18a]).

† The dynamical events are, of course, the interaction of the molecule, pair of molecules, etc., under consideration, with their environment. Clearly, the phase of the molecule, pair, etc., is not independent of the phase during a previous interval; it is the phase of the environment which is (assumed) independent of the phase during a previous interval.
(b) Despite the fact that the usual expansion parameters \( \rho \sigma^3 \) or \( \epsilon/kT \) are not useful in the liquid, there does exist a qualitatively different expansion parameter \( \tau_c/\tau \), where \( \tau_c \) is the lifetime of dynamical correlations and \( \tau \) is the time between dynamical events. The new parameter appears naturally because, when the surrounding medium has the property of propagating away or otherwise destroying dynamical correlations in the subsystem of interest, it is not pertinent to measure the strength of the interaction in terms relating to the spacing of the continuous spectrum of the Liouville operator of the surrounding medium. All that is pertinent in this case is the lifetime of dynamical correlations. For the case of a perturbation in momentum space, Rice and Allnatt [4] have shown that the lifetime of the dynamical correlation is an order of magnitude less than the time between dynamical events, thus justifying truncation of the coherence time expansion after terms in \( \tau_c/\tau \).

(c) The fundamental hypothesis of time smoothing is a natural expression of the nature of the coherence time expansion.

(d) The postulates of separability of intermolecular potential, instantaneous nature of rigid core collisions, and the nature of time smoothing all have interesting consequences for the development of Markovian kinetic equations from the exact non-Markovian statistical dynamical equations.

We have already mentioned the Rice-Allnatt kinetic equations [see (a) and (b)]. These were developed before the derivation of the coherence time expansion, using physical arguments with content substantially identical to the formal results of the coherence time analysis. For simplicity, we shall discuss the theory in intuitive terms.*

The theory of irreversible phenomena in liquids developed by Rice and Allnatt was, in the first instance, relevant to a model monatomic dense fluid in which the intermolecular potential has the form of a rigid core repulsion superimposed on an arbitrary soft potential. Subsequent analysis has shown that the extension of the model to include more realistic potentials presents no formal difficulty, provided that the repulsive potential is sufficiently short ranged.

What advantage results from separating the intermolecular potential into two parts and treating their effects separately? Quite simply, the difference in range and strength of the repulsive core and the soft potential allows the discussion of the molecular motion in terms of two

* A new derivation of these equations from a functional integral representation of nonequilibrium statistical mechanics has been given by Popielawski, Rice and Hurt [19a].
time scales: One corresponds to the large momentum and energy transfers which occur during a strongly repulsive encounter, while the other corresponds to the frequent small momentum and energy transfers which occur during the quasi-Brownian motion of a molecule in the superimposed soft force field of all the molecules in its surroundings. The short range of the strongly repulsive core implies that the first class of encounters are of short duration, so that the probability that a molecule undergoes such encounters with two or more others simultaneously is sufficiently small that it may be neglected. The introduction of the idealized rigid core representation for this class of encounters may thus be regarded as a formal device for restricting consideration to binary encounters (i.e., rigid core encounters between not more than two molecules). It has the additional advantage of considerably simplifying the mathematical details of the solutions of the equations but, we believe, without significantly affecting the numerical results [20].

Irreversibility is introduced into the analysis by the use of the Kirkwood hypothesis that a time interval $\tau$ exists such that the dynamical events occurring in one interval are independent of those in the preceding intervals. The dynamical event is identified as a rigid core encounter followed by erratic or quasi-Brownian motion in the fluctuating soft force field of the neighboring molecules. This identification is contingent upon the effectiveness of the quasi-Brownian motion in causing the environment to forget the momentum with which a molecule was rebounded after the rigid core encounter. This in turn implies that the relaxation time for the equilibrium of the momentum due to the soft force alone is much shorter than that due to rigid core encounters alone. It may be shown that this physical statement is supported by detailed calculation of the appropriate relaxation times for the motion considered.

The introduction of irreversibility in the manner described leads to a set of integrodifferential equations describing the evolution of the coarse-grained singlet $f^{(1)}(1)$, doublet $f^{(2)}(1, 2)$, etc., distribution functions. Details of the derivations may be found elsewhere [20]. Here, we merely quote the results:

(a) For the singlet distribution function, we find

$$D^{(1)}f^{(1)} = \sum_{i=1}^{3} J_{i}^{(1)} + \zeta_{p} A^{(1)}f^{(1)}$$

where

$$D^{(1)}f^{(1)} = \left( \frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_{1} \cdot \nabla_{1} + \mathbf{F}_{1}^{*} \cdot \nabla_{p_{1}} \right)f^{(1)}$$

$$A^{(1)}f^{(1)} = \nabla_{p_{1}} \cdot \left( \frac{1}{m} \mathbf{p}_{1} f^{(1)} + kT \nabla_{p_{1}} f^{(1)} \right)$$
and
\[ \mathbf{F}^*_1 = 0\langle \mathbf{F}^{(S)}_1 \rangle + (1)\mathbf{F}^{(S)}_1 \]  
(7)

If an external force \( \mathbf{X}_1 \) acts on molecule 1, and the fluid has a hydrodynamic velocity \( \mathbf{u} \), then it is easily shown that
\[
\mathcal{D}^{(1)}f^{(1)} = \left( \frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_1 \cdot \mathbf{v}_1 + (\mathbf{X}_1 + \mathbf{F}^*_1) \cdot \mathbf{v}_{p_1} \right) f^{(1)}  
\]  
(8a)
and
\[
\mathcal{A}^{(1)}f^{(1)} = \mathbf{v}_{p_1} \cdot \left( \frac{\mathbf{p}_1}{m} - \mathbf{u} \right) f^{(1)} + kT \mathbf{v}_{p_1} f^{(1)}  
\]  
(8b)

Of the remaining symbols in Eq. (5),
\[
J_1^{(1)} = \frac{g^{(2)}_0(R_1, \sigma)}{m} \int_{(k \cdot \mathbf{p}_{12} > 0)} [f^{(1)}(R_1, \mathbf{p}_1^*)f^{(1)}(R_1, \mathbf{p}_2^*) - f^{(1)}(R_1, \mathbf{p}_1)f^{(1)}(R_1, \mathbf{p}_2)] \mathbf{p}_{12}b \, db \, d\mathbf{p}_2  
\]  
(9a)
\[
J_2^{(1)} = \frac{\sigma g^{(2)}_0(R_1, \sigma)}{m} \int_{(k \cdot \mathbf{p}_{12} > 0)} [f^{(1)}(R_1, \mathbf{p}_1^*) \mathbf{k} \cdot \mathbf{v}_1 f^{(1)}(R_1, \mathbf{p}_2^*) + f^{(1)}(R_1, \mathbf{p}_1) \mathbf{k} \cdot \mathbf{v}_1 f^{(1)}(R_1, \mathbf{p}_2)] \mathbf{p}_{12}b \, db \, d\mathbf{p}_2  
\]  
(9b)
\[
J_3^{(1)} = \frac{\sigma}{2m} \mathbf{v}_1 g^{(2)}_0(R_1, \sigma) \cdot \int_{(k \cdot \mathbf{p}_{12} > 0)} \mathbf{k}[f^{(1)}(R_1, \mathbf{p}_1^*)f^{(1)}(R_1, \mathbf{p}_2^*) + f^{(1)}(R_1, \mathbf{p}_1)f^{(1)}(R_1, \mathbf{p}_2)] \mathbf{p}_{12}b \, db \, d\mathbf{p}_2  
\]  
(9c)

with \( g^{(2)}_0(R_1, \sigma) \) the local equilibrium pair correlation function at contact (taking the intermolecular potential to consist of a rigid core interaction plus a soft longer range interaction), \( \mathbf{k} \) is a unit vector along the line of centers when two molecules are in contact at \( |\mathbf{R}_{12}| = \sigma \), \( \sigma \) is the rigid core diameter, \( b \) the impact parameter, and \( \epsilon \) the azimuthal angle describing the binary encounter, and the asterisk refers to values of the parameters before collision. Finally,
\[
0\langle \mathbf{F}^{(S)}_1 \rangle = \rho \int \mathbf{F}^{(S)}_{12}(\mathbf{R}_{12}) g^{(2)}_0(\mathbf{R}_{12}) \, d\mathbf{R}_{12}  
\]  
(10)
\[
(1)\mathbf{F}^{(S)}_1 = \rho \int \mathbf{F}^{(S)}_{12}(\mathbf{R}_{12}) g^{(2)}_1(\mathbf{R}_1, \mathbf{R}_2) \, d\mathbf{R}_{12}  
\]
where \( \rho = (N - 1)/V \). It must be noted that Eq. (14) is valid only for the case that the friction coefficient \( \zeta_5 \) is independent of the particle
momentum. This is not in general true, but the full equation corre-
sponding to Eq. (15) which is derived from the Rice-Allnatt theory
is of such complex structure that analytic solutions are not known. In
place of this general equation, Rice and Allnatt adopt, as a first approx-
imation, the alternative form of the equation (which still yields the
Maxwellian equilibrium momentum distribution) with constant friction
coefficient. In this case the solutions to the kinetic equation may be
obtained without difficulty using Kihara functions [21].

It should also be noted that the weak coupling part of the equation
derived by these methods is identical with that derived by Prigogine [17].

Of course, the general theory also leads to a formal expression for the
friction coefficient. Indeed, the momentum-dependent friction tensor
corresponding to the weak coupling Fokker-Planck operator is found to be

\[
\zeta = \frac{1}{kT_\tau} \int_0^\infty \int_0^\infty F^{(S)}(r) F^{(S)}(q) \left( R^{(N)}(r) + \frac{s'}{m} p^{(N)}(q) \right)
\cdot f^{(N-1)}(r_{N-1} | r_1) d\Gamma_{N-1} d\tau ds ds
\]

(11)

with \( R^{(N)} \) and \( p^{(N)} \) the position and momentum vectors for \( N \) molecules.

(b) For the doublet distribution function, if we denote the hydro-
dynamic flow velocity and temperature at \( R_i \) by \( \mathbf{u}_i \) and \( T_i \), respectively,
the final form is

\[
\mathcal{D} \mathcal{f}^{(2)} = \sum_{i=1}^3 J_i^{(2)} + \sum_{i=1}^2 \zeta_i(R_i) \cdot \mathcal{A}_i^{(1)} \mathcal{f}^{(2)}
\]

(12)

where the \( J_i^{(2)} \) are given by

(i) \( J_1^{(2)} = J_1^{(3)}(1) + J_1^{(2)}(2) \)

\[
= \frac{1}{m} g^{(2)}(R_1, R_2) g(\sigma)
\times \left[ \int_{(k,p_{23}>0,\text{sym})} \left[ f^{(3)}(R_1, p_1^+; R_2, p_2; R_1, p_3^*; t) - f^{(3)}(R_1, p_1; R_2, p_2^*; R_1, p_3; t) \right] p_{13}^b db de dp_3 \\
+ \int_{(k,p_{23}>0,\text{sym})} \left[ f^{(3)}(R_1, p_1; R_2, p_2^*; R_2, p_3^*; t) - f^{(3)}(R_1, p_1^+; R_2, p_2; R_2, p_3^*; t) \right] p_{23}^b db de dp_3 \right]
\]

(13a)
(ii) \[ J_2^{(2)} = J_2^{(2)}(1) + J_2^{(2)}(2) \]
\[ = \frac{\sigma}{m} g^{(2)}(\mathbf{R}_1, \mathbf{R}_2) g(\sigma) \]
\[ \times \left[ \int_{(k \cdot p_{13} > 0; \text{sym})} \left[ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2) k \cdot \mathbf{V}_1 f^{(1)}(\mathbf{R}_1, \mathbf{p}'_3) \\
+ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2) k \cdot \mathbf{V}_1 f^{(1)}(\mathbf{R}_1, \mathbf{p}_3) \right] p_{13} b \, db \, dp_3 \right. \]
\[ + \int_{(k \cdot p_{23} > 0; \text{sym})} \left[ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2) k \cdot \mathbf{V}_2 f^{(1)}(\mathbf{R}_2, \mathbf{p}'_3) \\
+ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2) k \cdot \mathbf{V}_2 f^{(1)}(\mathbf{R}_2, \mathbf{p}_3) \right] p_{23} b \, db \, dp_3 \right] \] (13b)

(iii) \[ J_3^{(2)} = J_3^{(2)}(1) + J_3^{(2)}(2) \]
\[ = \frac{\sigma}{2m} g^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \]
\[ \times \left[ \int_{(k \cdot p_{13} > 0; \text{sym})} \left[ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1^*) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2) f^{(1)}(\mathbf{R}_1, \mathbf{p}'_3^*) \right. \\
+ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1^*) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2) f^{(1)}(\mathbf{R}_1, \mathbf{p}_3) \] \[ \times k \cdot \mathbf{V}_1 g^{(2)}(\mathbf{R}_1, \sigma) p_{13} b \, db \, dp_3 \right. \]
\[ + \int_{(k \cdot p_{23} > 0; \text{sym})} \left[ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1^*) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2^*) f^{(1)}(\mathbf{R}_2, \mathbf{p}'_3) \\
+ f^{(1)}(\mathbf{R}_1, \mathbf{p}_1^*) f^{(1)}(\mathbf{R}_2, \mathbf{p}_2^*) f^{(1)}(\mathbf{R}_2, \mathbf{p}_3) \] \[ \left. \times k \cdot \mathbf{V}_2 g^{(2)}(\mathbf{R}_2, \sigma) p_{23} b \, db \, dp_3 \right] \] (13c)

and
\[ \mathcal{S}^{(2)} f^{(2)} = \left[ \frac{\partial}{\partial t} + \sum_{i=1}^{2} \left( \frac{1}{m} \mathbf{p}_i \cdot \mathbf{V}_i + \mathbf{F}_i^{(2)} \cdot \mathbf{V}_i \right) \right] f^{(2)} \] (14)
\[ \mathcal{S}^{(1)} f^{(2)} = \mathbf{V}_{p_i} \cdot \left[ \left( \frac{1}{m} \mathbf{p}_i - \mathbf{u}_i \right) + kT_i \mathbf{V}_p \right] f^{(2)} \] (15)
\[ \mathbf{F}_i^{(2)} = (2)\mathbf{F}_i^{(H)} + (2)\mathbf{F}_i^{(S)} \] (16)
\[ (2)\mathbf{F}_i^{(R)} = (2)\mathbf{F}_i^{(R)} + (2)\mathbf{F}_i^{(R)^*} \] where \( R = H \) or \( S \) (17)

The kinetic equations (5) and (12) may be solved analytically when there are only small deviations from equilibrium. The solutions, which
depend on the temperature gradient, velocity gradient, etc., may then be used to compute the several transport coefficients. The results are as follows.

(a) Thermal conductance:

\[
\kappa = \kappa_K + \kappa_e(\sigma) + \kappa_v(R > \sigma)
\]

\[
\kappa_K = \frac{75k^2T}{32\sigma g(\sigma)} \left[ \frac{1 + (2\pi \sigma^3/5) g(\sigma)}{\Omega^{(2,2)} + [45\xi_S/16\sigma g(\sigma)]} \right]
\]

\[
\kappa_v(R > \sigma) = \frac{\pi k T \rho^2}{3\xi_S} \int_{R_1}^\infty R_{12} \left( R_{12} \frac{d u}{d R_{12}} - u \right) \frac{d R_{12}}{R_{12}} \left( \frac{\sigma^3}{g(\sigma)} \right)
\]

\[
\eta = \eta_K + \sum_{i=1}^{3} \eta^{(i)}(\sigma) + \eta_v(R > \sigma)
\]

\[
\eta_K = \frac{5kT}{8g(\sigma)} \left[ \frac{1 + (4\pi \sigma^3 g(\sigma)/15\nu)}{\Omega^{(2,2)} + (5\xi_S/4\sigma g(\sigma))] \right]
\]

\[
\eta^{(1)}_v(\sigma) = \frac{5kT}{8g(\sigma)} \left( \frac{2\pi \sigma^3 g(\sigma)}{15} \right) \left[ 1 + \frac{4\pi \sigma^3}{15} g(\sigma) \right] D
\]

\[
\eta^{(2)}_v(\sigma) = \frac{8\pi \rho \sigma^3 g(\sigma) kT}{15 \xi_S}
\]

\[
\eta^{(3)}_v(\sigma) = -\frac{37}{70} \left( \frac{2\pi \sigma^3}{15} \right) \rho g(\sigma) \xi_S \psi_2(\sigma)
\]

\[
D = \left[ \Omega^{(2,2)} + \frac{5\xi_S}{8\sigma g(\sigma)} \right]^{-1} \times \left\{ 1 + \frac{4\Omega^{(2,2)}}{4\Omega^{(2,2)} + [5\xi_S/\sigma g(\sigma)]} \right\}
\]

\[
\eta_v(R > \sigma) = \frac{\pi \xi_S \rho^2}{15kT} \int_{R}^\infty R^3 \frac{d R}{d R} \Omega^{(2,2)}(R) \psi_2(R) d R
\]
with the function $\psi_2(R)$ obtained as the solution to the differential equation

$$\frac{d}{dR_{12}} \left( R_{12}^{2} g^{(2)}_{12} \frac{d\psi_2}{dR_{12}} \right) - 6 g^{(3)}_{12} \psi_2 = R_{12}^{3} \frac{d g^{(2)}_{0}}{dR_{12}}$$  \hspace{1cm} (22)$$

with boundary conditions

$$\lim_{R_{12} \to +\infty} \psi_2(R_{12}) = 0$$

$$\lim_{R_{12} \to +\infty} R_{12}^{2} g^{(2)}_{12} \frac{d\psi_2}{dR_{12}} = 0$$  \hspace{1cm} (23)$$

(c) Bulk viscosity*:

$$\phi = \sum_{i=1}^{3} \phi^{(i)}(\sigma) + \phi_v (R > \sigma)$$  \hspace{1cm} (24)$$

$$\phi_v^{(1)}(\sigma) = 0$$

$$\phi_v^{(2)}(\sigma) = \frac{2}{3} \eta_v^{(2)}$$

$$\phi_v^{(3)}(\sigma) = \frac{2 \pi \rho \sigma^3}{15} \rho g(\sigma) \frac{4 \psi_2(\sigma) - 35 \psi_0(\sigma)}{42}$$

$$\phi_v (R > \sigma) = \frac{\pi \zeta_S}{9 kT} \rho^2 \int_{\sigma}^{\infty} u'(R) g^{(2)}_{0}(R) \psi_0(R) R^3 dR$$  \hspace{1cm} (25)$$

(d) Ion mobility:

$$\mu_+ = \frac{q}{\frac{2}{3} \rho g(\sigma) \left( \frac{2 \pi m_i^2 kT}{m + m_i} \right)^{1/2} + \zeta_S}$$  \hspace{1cm} (26)$$

where $q$ is the charge on the ion, $m_i$ the mass of the ion, and the appropriate value of $\sigma$ is for the ion-molecule core interaction.

(e) The friction coefficient $\zeta_S$, which appears in all the preceding formulas, has not yet been computed with comparable accuracy. Three different theoretical estimates are:

(i) $\zeta_S^2 = \frac{\rho m}{3} \int \nabla^2 u(R) g^{(2)}(R) d^3R$  \hspace{1cm} (27a)$$

(ii) $\zeta_S = -\frac{p}{3} \left( \frac{\pi m_i}{kT} \right)^{1/2} (2\pi)^{-2} \int k^3 \hat{G}(k) dk$

* There is no kinetic contribution to the bulk viscosity; in other words: $\phi_k = 0$. 
with

\[ \hat{V}(k) = \int u(R) \exp(ik \cdot R) \, d^3R \]  

(27b)

\[ \hat{G}(k) = \int (g^{(0)}(R) - 1) \exp(ik \cdot R) \, d^3R \]  

(27c)

Another estimate of the friction coefficient can be derived from the Kirkwood expression [5]

\[ \zeta = \frac{1}{3kT} \int_0^\tau ds \langle F(t) \cdot F(t + s) \rangle \]  

(28a)

which is the time-integrated force autocorrelation function, this function being the equilibrium ensemble average of the product of the force on a particle at time \( t \) and that on the particle at time \( t + s \). Lebowitz and Rubin [22] and Résoibois and Davis [23] have given rigorous derivations of this expression in the description of the motion of a Brownian particle. On the other hand the use of (28a) for the description of self-diffusion of molecules of similar masses must be considered to be an approximation whose utility will be determined by comparison between experiment and theory.

Splitting the force into two parts, \( F^{(H)} \), a hard core interaction, and \( F^{(S)} \), a soft force, one can write the friction coefficient in the form

\[ \zeta = \zeta_H + \zeta_S + \zeta_{S,H} \]

\[ = \frac{1}{3kT} \left\{ \int_0^\tau ds \langle F^{(H)}(t) \cdot F^{(H)}(t + s) \rangle \right. \]

\[ + \int_0^\tau ds \langle F(t) \cdot F^{(S)}(t + s) \rangle + \int_0^\tau ds \langle F^{(S)}(t) \cdot F^{(H)}(t + s) \rangle \right\}. \]  

(28b)

The term \( \zeta_H \) is the hard core friction coefficient and in explicit form is found in the denominator of Eq. (26). Helfand [24] has evaluated \( \zeta_S \) in the linear trajectory approximation, which is an evaluation of the weak coupling friction tensor given by Eq. (11). His result is that given in Eq. (27b). Recently, Davis and Palyvos [25, 26] have evaluated \( \zeta_{S,H} \) in the linear trajectory approximation.

The combination of the hard core result for \( \zeta_H \), Helfand's formula for
\( \zeta \), and Davis and Palyvos' formula for \( \zeta_{S,H} \) yields the friction coefficient for a particle of species \( \alpha \) in a \( \nu \)-component mixture:

\[
\zeta = \sum_{\gamma=1}^{\nu} \frac{8\sigma_{\alpha\gamma}^{2} \tau_{\alpha\gamma}}{\rho_{\gamma}} \left( \frac{2\pi m_{\alpha} m_{\gamma} kT}{m_{\alpha} + m_{\gamma}} \right)^{1/2} \]

\[- \sum_{\gamma=1}^{\nu} \frac{\rho_{\gamma}}{\left( m_{\alpha} + m_{\gamma} \right)^{1/2}} \int_{0}^{\infty} k^{3} \overline{\varphi}_{\alpha\gamma}(k) G_{\alpha\gamma}(k) \, dk \]

\[- \sum_{\gamma=1}^{\nu} \frac{8\sigma_{\alpha\gamma}^{2} \xi_{\alpha\gamma}^{(q)}}{\rho_{\gamma}} \left[ 2\pi \left( \frac{m_{\alpha} m_{\gamma}}{m_{\alpha} + m_{\gamma}} \right) kT \right]^{1/2} j_{\alpha\gamma}^{(q)} \]

\[- \int_{0}^{\infty} \frac{1}{4\pi \sigma_{\alpha\gamma}^2 kT} \int_{0}^{\infty} dk d\mathbf{l} \frac{1}{l^3k} \left[ \rho_{\gamma} \cos (\sigma_{\alpha\gamma}) \right] \overline{\varphi}_{\alpha\gamma}(k) G_{\alpha\gamma}(l) G_{\alpha\gamma}(|k - 1|) \]

In Eq. \( (29a) \) the \( j_{\alpha\gamma} \) are the dimensionless quantities:

\[
j_{\alpha\gamma}^{(q)} = \frac{1}{4\pi \sigma_{\alpha\gamma}^2 kT} \int_{0}^{\infty} dk (k \sigma_{\alpha\gamma} \cos k \sigma_{\alpha\gamma} - \sin k \sigma_{\alpha\gamma}) \overline{\varphi}_{\alpha\gamma}^{S}(k) \]

\[
j_{\alpha\gamma}^{(q)} = \frac{1}{4\pi \sigma_{\alpha\gamma}^2 kT} \int_{0}^{\infty} dk d\mathbf{l} \frac{1}{l^3k} \left[ \rho_{\gamma} \cos (\sigma_{\alpha\gamma}) \right] \overline{\varphi}_{\alpha\gamma}(k) G_{\alpha\gamma}(l) G_{\alpha\gamma}(|k - 1|) \]

A discussion of the above formulas for the friction coefficients is deferred to Section 3.

2.3. Formal Theories of Transport Phenomena

2.3.1. Prigogine and Co-Workers

In the preceding section we have briefly outlined a kinetic theory of liquids. Of particular importance in the analysis is the method of defining a dynamical event and of introducing the element of irreversibility which transforms the description of the system in terms of time reversible microscopic equations of motion into a description in terms of time irreversible macroscopic flow equations. Although time smoothing has proved useful and successful, it is by no means the only manner (nor the most elegant) of treating transport phenomena. It is not our purpose to make an elaborate comparison of the various theoretical approaches that have been proposed. For our purposes it is sufficient to remark that in the steady state all the extant statistical theories of transport lead to the same cluster expansion \( [13-15, 27-31] \) of the integrodifferential equation defining the behavior of \( f^{(n)} \) and also to the same autocorrelation function definitions of the transport coefficients \( [32-35] \). It is our opinion that at present the only analysis which can be \textit{practically} applied to the
study of liquids is that discussed in the preceding section. Nevertheless, there remain a number of questions of importance which cannot be answered within the framework of the formalism we have used: These include the nature of the approach to equilibrium, the possible role of non-Markovian effects, verification and clarification of the time coarse-graining hypothesis, etc.

Recent theoretical advances in the statistical mechanics of nonequilibrium systems are dominated by the studies of Prigogine [17] and co-workers (Balescu [36], Résibois [37]) and by the contributions of Zwanzig [18c]. Any discussion of the approach to equilibrium must make some mention of this work even though the formalism, at the present time, is useful only for dilute or weakly coupled systems. This statement does not imply anything more than that the formalism is hard to use for strongly interacting systems (such as the short-range repulsive interactions in a liquid). In Section 2.3.2 we shall discuss a weak coupling theory based on the Prigogine formalism.

It is possible to establish some formal connections between the general theory of nonequilibrium statistical mechanics and the more specific techniques and concepts employed by Rice and Allnatt [4]. To achieve this end, it is necessary to examine two different formalisms: the autocorrelation function approach of Green [32], Kubo [33], and others, and the approach of Prigogine [17] and co-workers (Balescu [36], Résibois [37]) based on solution of the Liouville equation using the techniques of infinite order perturbation theory. These two formalisms may be demonstrated to be equivalent for the purpose of calculating transport coefficients [34].

The basic idea of the autocorrelation function analysis is that transport coefficients may be expressed as generalized susceptibilities defining the response of the system to some macroscopic constraint (such as a temperature gradient). The various published derivations all lead to the same formal expressions for the transport coefficients associated with the various fluxes. Unlike the kinetic analysis, wherein a quasi-stationary distribution function results from the balance between streaming in phase space and molecular interaction processes, in the autocorrelation function formalism the transport process arises from the decay of fluctuations in an equilibrium ensemble. Of course, the analysis is purely formal in the sense that it leads to expressions requiring solutions of the N-body problem before evaluation can be completed. At present, the autocorrelation function method cannot be used (practically) to describe strongly interacting systems, such as the liquid phase, without auxiliary consideration of kinetic equations defining the behavior of the distribution function.
The basis of the analysis of Prigogine and co-workers lies in the Fourier decomposition of the $N$-body distribution function, $f^{(N)}$, and the classification of terms which appear in the decomposition according to powers of $t$, $N/V$, and $\lambda$, where $\lambda$ is the coupling constant of the intermolecular potential energy. In this formalism the Liouville equation takes a form which describes the transitions between different distributions of wave vectors; the transitions are generated by the interactions between the molecules, and the distributions of wave vectors are the respective Fourier space representations of the distribution function. The equations are naturally ordered in a sequence which counts the number of nonzero wave vectors. To evaluate the terms in this representation, Prigogine and Balescu have invented a diagrammatic notation [17, 36].

The general technique used to obtain a kinetic equation (i.e., an integrodifferential equation describing the evolution of a reduced distribution function) is to sum classes of diagrams ordered in part according to the number of nonzero wave vectors. (A function of the coordinates of $n$ molecules is expressed in terms of a Fourier transform, which is a function of $n$ wave vectors, denoted by $\rho_n$.) Successively higher approximations are obtained by summing the contributions of terms with successively larger numbers of nonzero wave vectors and more complicated sequences of nonvanishing sets. This procedure of diagram selection and subsequent construction of reduced asymptotic equations constitutes the most elegant discussion of the approach to equilibrium yet devised. The salient features are the following. First, the asymptotic evaluation of the matrix elements by summing diagrams is only valid for large systems for which $N \rightarrow \infty$, $V \rightarrow \infty$, but $N/V$ remains constant. Second, the approach to equilibrium appears in this formalism as a cascade mechanism by which the time dependence of a given Fourier component of the distribution function is related to different order Fourier components (i.e., different numbers of nonzero wave vectors). In general, the rate of change of any $\rho_n$ is expressed in terms of the initial correlations $\rho_{n'}$, and is a sum over all transitions giving as a final outcome the transition $n' \rightarrow n$. In particular, the rate of change of $\rho_0$ (which is the velocity distribution function) depends upon $\rho_0$ through all possible sequences of transitions $0 \rightarrow n \rightarrow n' \rightarrow \cdots \rightarrow 0$, and upon the initial correlations $\rho_{n'}$, through all possible sequences $n' \rightarrow n'' \rightarrow \cdots \rightarrow 0$. The operator representing the former set of transitions is called the diagonal fragment, and that representing the latter set is called the destruction fragment. The kinetic equations so derived are strictly irreversible in the sense that the Poincaré recurrence time is rejected to infinity by the process of taking the limit $N \rightarrow \infty$. 
TRANSPORT PHENOMENA IN SIMPLE LIQUIDS 279

$V \to \infty$, $N/V$ constant. However, the equations are mechanically reversible. Although the destruction fragment tends to zero rapidly compared to the approach to equilibrium, if at any time $t$ all the velocities are reversed, then at time $2t$ the destruction fragment reattains its initial value.

By the use of operator techniques to solve the Liouville equation, Prigogine and Résibois have shown that [38]

\begin{equation}
\frac{\partial \rho_0(t)}{\partial t} = D_0(t, \rho(\omega)) + \int_0^t G_{00}(t - t') \rho_0(t') \, dt'
\end{equation}

(30)

The exact master equation describes the time evolution of $\rho_0$ for all time. The structure of the equation is very simple: The inhomogeneous term $D_0$ gives the contribution, at time $t$, of the initially excited Fourier components which through interaction decay toward a state with no correlations; the second term has a non-Markovian structure so that $\partial \rho_0(t)/\partial t$ depends upon $\rho_0(t')$ for times $t' < t$, and is representative of the fact that $\rho_0$ in general changes during a collision. Note that all the effects of the initial correlations and initial conditions appear in the term $D_0$, while for the case we are considering $G_{00}$ refers only to diagonal fragments. A kinetic equation for the nondiagonal Fourier components, $\rho_{ik}(t)$, may also be obtained. For this and other applications the reader is referred to the monograph by Prigogine [17] and the original literature.

The first use to which the general master equation can be put is the examination of kinetic equations in the limit $t \to \infty$. In the transition to the limit it is seen that not only do all the effects contained in $D_0$ wash out, but also that all effects arising from the finite duration of the binary encounters still do not prevent the kinetic equation being Markovian in the limit $t \to \infty$. For example, the phenomenological transport coefficients involve only the asymptotic cross sections, and no terms appear which are related to the duration of an encounter, except in the case of the bulk viscosity.

The appearance of the time convolution in the generalized master equation specifically includes contributions to $\partial \rho_0(t)/\partial t$ from $\rho_0(t')$ for $t' \leq t$, with a weight $G_{00}(t - t')$. The behavior of $G_{00}(t - t')$ is determined by the intermolecular forces, density, etc., but not by the initial state of the system. Thus, the role of the convolution as such will only be important for times of the order of the interaction time $\tau_e$, giving rise to transient effects. For $t \gg \tau_e$, the velocity distribution will vary only a little during $\tau_e$, and the operator

\[ \int_0^t G_{00}(t - t') \, dt' \]
will be approximately independent of \( t \). The kinetic equation will then have the Markovian form

\[
\frac{\partial \rho_0}{\partial t} = \mathcal{G}_{00} \rho_0
\]

(31)

where the operator \( \mathcal{G}_{00} \) is given by

\[
\mathcal{G}_{00} = \int_0^\infty G_{00}(t - t') \, dt'
\]

(32)

At this stage, correlations over distances of the order \( (p/m)\tau_c \) will have been destroyed and the system will be evolving in the kinetic regime.

This description bears a considerable resemblance to the role which was assigned to the time coarse graining in the Kirkwood analysis, where, in order to develop an explicit representation of \( \mathcal{G}_{00} \), a mechanism for the interactions was proposed. Equally important is the difference between the coarse graining proposed by Kirkwood and the way in which \( \mathcal{G}_{00} \) is reached. The simple form of coarse graining involves an unweighted time average, while \( \mathcal{G}_{00} \) is the result of a complex weighting determined by the nature of the interaction. It is possible that a more penetrating analysis than that given in Section 2.2 of the way in which a Markovian process can be extracted from a high order non-Markovian process would throw some light upon more subtle relationships between the two theories.

The method used to obtain a master equation for the velocity distribution function may also be used, with slight extension, to describe the time evolution of the molecular correlations. Again, a non-Markovian equation is found to hold for all \( t \), reducing to a Markovian equation in the limit \( t \to \infty \).

In brief, then:

1. The general kinetic equation is non-Markovian.
2. For times long compared to the duration of an encounter (and to other characteristic times in more general cases) it reduces to a Markovian equation, which may or may not require correction for effects due to the finite duration of an encounter.
3. For quasi-stationary situations, only the asymptotic form of the diagonal fragment enters the collision operator.

Thus, the form of the kinetic equation depends on the type of process being described and on the time scale of interest.

It is interesting to compare the Kirkwood coarse-graining hypothesis with the neglect of the initial correlations described by \( \mathcal{D}_0 \) and the transition to Markovian behavior. First, it should be noted that \( \mathcal{D}_0 \) tends
to zero as \( t \) increases for the reason that correlations of finite extent in the initial state can only persist for a finite time. Indeed, if the range of the correlations is of molecular dimensions, then the lifetime of the initial correlations is of the order of an interaction time.* Second, the effect of the non-Markovian kernel is to connect the distribution function to itself over times of the order of the duration of an encounter. Now the fundamental idea involved in the use of coarse graining is that the dynamical event in \( \tau \) is independent of prior dynamical events. This means that on the time scale chosen \( \mathcal{D}_0 \) must vanish, and that the time integral involving \( G_{00}(\tau) \) must approach a limit independent of \( \tau \).

Consider the first requirement. In Section 2.2 we remarked that if the distribution function returned to the form characteristic of the local environment on a time scale short compared to \( \tau \), then the process defined by time smoothing became a Markovian process. Moreover, for the case of a perturbation in momentum space, Rice and Allnatt [4] have shown that the singlet kinetic equation is consistent with this condition. It is clear that, in effect, the calculation of the relaxation time for a perturbation in momentum space is equivalent to the calculation of the lifetime of the correlations in a specified initial state. The consistency in this regard shows that \( \mathcal{D}_0 \) can be neglected under the conditions described by the Rice-Allnatt equation, and that the use of time coarse graining does lead, as expected, to \( \mathcal{D}_0 = 0 \). Of course this is shown only for a special case, but the physical description is clear enough that the argument can be extended. For some states \( \mathcal{D}_0 \) cannot be neglected (spin-echo experiment) and each situation must be separately analyzed. It may be concluded, however, that for the liquids studied in this review coarse graining does lead to an equation from which all information about the initial correlations has been removed.

Consider now the second requirement. For the case of a stationary state, such as is characteristic of the study of steady state transport phenomena, it has been shown that the effects of finite duration of an interaction do not appear and only the asymptotic form of the interaction operator is required. The general theorem is proved using a Taylor expansion of the distribution function about some origin in time and noting that the correction to the asymptotic zero duration collision operator arises from the first time derivative of the distribution function. Under conditions characterizing a stationary state the derivative term may be neglected, leading to the result cited.

There are many other general theorems which may be proven within the formalism outlined. For example, it may be shown that the Maxwell-
Boltzmann distribution is a stationary solution of the asymptotic master equation, that the time-dependent correlations approach the Mayer equilibrium correlations [17]. In addition, connections between the general theory and other theories are established through demonstrating the identity of all terms in the cluster expansion of the integrodifferential equation defining the properties of \( f^{(1)} \), and by showing that the autocorrelation function formulas for the transport coefficients are consistent with the general theory. For these and other results the reader is referred to the literature.

An alternative to the analysis described in the first part of this section has developed concurrently with it. Stimulated perhaps by the expression for the friction coefficient* obtained by Kirkwood [5], which is essentially the time integral of a force autocorrelation function, the essential features of this formalism were first proposed by Green [32]. The transport coefficients which appear in the correlation function formalism fall into two distinct classes. Namely, those which are associated with the response of a system to externally applied conservative forces, and those which cannot be so associated. Of the former type, rigorous expressions for the transport coefficients were first obtained by Kubo [33].† An obvious example is the electrical conductivity. The latter class includes transport processes which result from nonuniformities in a system, of which an example is the transport of momentum in a nonuniform velocity field (viscosity coefficient). In this case, the difficulty of representing nonmechanical disturbances in terms of some sort of perturbation to the system Hamiltonian has led to a number of alternative formulations of the problem and no rigorous derivation of the expressions for the transport coefficients has yet been given [24, 32, 35, 39–46].

Without describing the details of the derivations, we merely quote the formulas [47]:

\[
D = \frac{1}{3m^2} \int_0^\infty \langle p_i(0) \cdot p_i(s) \rangle \, ds \\
\kappa = \frac{1}{3VT} \int_0^\infty \langle J_i(0) \cdot J_i(s) \rangle \, ds \\
\eta = \frac{1}{VT} \int_0^\infty \langle J_i^{\alpha\nu}(0) J_i^{\alpha\nu}(s) \rangle \, ds \\
\phi = \frac{1}{VT} \int_0^\infty \langle J_i^{\alpha\sigma}(0) J_i^{\alpha\sigma}(s) \rangle \, ds
\]

* In the present context the friction coefficient should be regarded as a diffusion (i.e., transport) coefficient in momentum space.
† Expressions for transport coefficients of both types are often referred to as Kubo relations.
with

$$J_E = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} \cdot 1 + \frac{1}{2} \sum_{\neq i}^{N} (u_{ij} \cdot 1 - R_{ij} \cdot v_{ij}) \right] \cdot \frac{P_i}{m}$$

$$J_P = \sum_{i=1}^{N} \left( \frac{1}{m} \cdot P_i - \frac{1}{2} \sum_{\neq i}^{N} \cdot R_{ij} \cdot v_{ij} \cdot v_{ij} \right) - 1 \cdot P \cdot 1$$

We therefore see that the general theory of irreversibility quantifies and clarifies our understanding of the nature of dissipative processes, and also confirms the qualitative notions introduced in earlier work. The enormous advantage of the general theory lies in the quantification scheme, as it now appears possible to describe the time evolution of distribution functions (and thereby both microscopic and macroscopic of matter) for all times. It is to be expected that thereby many new phenomena will be discovered, and many well-known phenomena will be better understood and more fundamentally interpreted.

2.3.2. The Prigogine-Nicolis-Misguich Local Equilibrium Theory*

Using the formalism of Prigogine and co-workers, Prigogine, Nicolis and Misguich [48, 49, 89] have derived an integral equation for the deviation of the doublet distribution function from local equilibrium under the assumption that the singlet distribution function remains in local equilibrium. The doublet distribution function derived under this assumption suffices for calculating part of the potential energy contributions to the transport of energy and momentum in a fluid. Neglecting deviations of the singlet distribution function from local equilibrium, one not only ignores the kinetic (or piggyback) contribution to transport but also a potential energy contribution arising from distortions of the singlet distribution function. Although the neglected contributions may be small for a substance near its melting point, there is no reason to believe that they are small enough to be discarded throughout the liquid range. That one may not neglect the kinetic and distortion terms for much of the temperature range of a liquid is suggested by calculations based on the Rice-Allnatt theory and simple theories such as those for the hard sphere and the square well models.

The solution to the integral equation derived by PNM has not been obtained in general, since in its general form the equation still represents the $N$-body problem for dense random systems. However, resorting to

* Referred to hereafter as PNM.
an approximation closely related to the linear trajectory approximation, 
PNM obtained an explicit solution of their equation. This approximation—introduced by Ross [50] in his perturbation theory of the Fokker-
Planck equation, by Helfand [24] in evaluating the friction coefficient, and 
by Rice and Allnatt [4] in handling the soft potential contribution to the 
kinetic equations—essentially states that for the purpose of calculating 
the time integral of certain autocorrelation functions one can replace the 
actual trajectories of interacting molecules with linear trajectories. This 
approximation is intuitively reasonable when the average interactions 
are weak or slowly varying; however, the model certainly becomes more 
questionable for systems with short-range strongly repulsive interactions. 
In this case it would require further justification (see below).

The soft force contributions to the coefficients as obtained from the 
PNM theory may be summarized as follows:

(a) Thermal conductivity

\[ \kappa^S = \frac{4}{3} \pi^4 \rho^2 \left( \frac{\pi k T}{m} \right)^{1/2} \left[ \left( T \frac{\partial}{\partial T} - 2 \frac{h^\nu}{kT} \right) (6W_1 + W_2) - 5W_1 + \frac{7}{2} W_2 + W_3 \right] \]  

(34a)

(b) Shear viscosity

\[ \eta^S = \frac{8}{15} \pi^4 \rho^2 \left( \frac{\pi m}{kT} \right)^{1/2} [3W_2 + W_3] \]  

(34b)

(c) Bulk viscosity

\[ \phi^S = \frac{8}{9} \pi^4 \rho^2 \left( \frac{\pi m}{kT} \right)^{1/2} \left[ 4W_2 + W_3 + 3 \left( XT \frac{\partial}{\partial T} + \frac{1}{2} X' \right) (3W_1 + W_2) \right] \]  

(34c)

with the definitions

\[ W_n = \int_0^\infty dk \, \hat{G}(k) k^n \frac{\partial^{n-1}}{\partial k^{n-1}} \hat{V}^{(S)}(k), \quad X = \frac{1}{\rho} \left( \frac{\partial p}{\partial e} \right)_\rho, \quad X' = X - \frac{4}{3} \]

Here \( h^\nu \) denotes the potential part of the enthalpy per particle, \( p \) the 
equilibrium pressure, and \( e \) the equilibrium mean energy per particle.

Misguich has also obtained formulas for the contribution of the hard 
core part of the interaction potential. These formulas are

(a) Thermal conductivity

\[ \kappa^H = \kappa^0 \left\{ g^{(2)}(\sigma) + S + \frac{1}{16} \int_0^\infty dx \, x \left[ P_2(x) T \frac{\partial}{\partial T} g^{(3)}(x) \right. \right. \]

\[ \left. + \left( g^{(2)}(x) - 1 \right) (4P_4(x) - \frac{1}{2} \left( 1 + 4 \frac{h^\nu}{kT} \right) P_2(x)) \right\} \]  

(34d)
(b) Shear viscosity

$$\eta^H = \eta^0 \left[ g^{(2)}(x) + S + \frac{1}{8} \int_1^\infty dx \, x \left[ g^{(2)}(x) - 1 \right] \left( 3P_4(x) - P_3(x) \right) \right]$$  \hspace{1cm} (34e)

(c) Bulk viscosity

$$\phi^H = \phi^0 \left[ g^{(2)}(x) + S + \frac{3}{16} \int_1^\infty dx \, xP_3(x) \left[ XT \frac{\partial}{\partial T} - \frac{1}{2} X' \right] \left( g^{(2)}(x) - 1 \right) \right]$$  \hspace{1cm} (34f)

where the following definitions have been introduced:

$$\tilde{\eta} = \frac{\kappa^0}{\kappa} = \frac{m}{kT}, \quad \kappa^0 = \frac{3}{8} \rho^2 \sigma^4 (\pi m h T)^{1/2}$$  \hspace{1cm} (34g)

$$P_n(x) = \int_{-1}^0 d\xi \, \xi^n [\xi^2 - 1 + \xi^2]^{-1/2}$$  \hspace{1cm} (34h)

$$S = -\frac{1}{2} \left[ g^{(2)}(x) - 1 \right] - \frac{1}{16} \int_1^\infty dx \, x \left[ g^{(2)}(x) - 1 \right] \frac{\partial}{\partial x} \left[ P_3(x) - P_4(x) \right]$$  \hspace{1cm} (34i)

The first term in each of the Eqs. (34d)–(34f) is proportional to the "contact" pair correlation function, and can therefore be considered as an Enskog-type contribution. The two other terms represent the cross contributions between the hard and soft parts of the force and are expected to be small (it has been verified, in some specific cases, that they represent about 2% of the total shear viscosity). Similar expressions can be derived for the contribution to the bulk viscosity and the thermal conductivity.

A comparison of experiment and theory, to be discussed in more detail in Section 3, indicates that for simple liquids the PNM theory predicts for argon about 75 to 85% of the observed shear viscosity, about 30 to 80% of the observed bulk viscosity, and about 40 to 60% of the thermal conductivity.

2.3.3. The Berne-Boon-Rice derivation of the Transport Coefficients from the Autocorrelation Function*

It has been recently shown [51] that the time evolution of the autocorrelation function of any phase function $U(\Gamma_N ; t)$ can be obtained by straightforward means from the autocorrelation function

$$\psi(t) = \langle U(\Gamma_N ; 0) \, U(\Gamma_N ; t) \rangle$$

* Hereafter referred to as BBR (see Berne et al. [51], Boon et al. [52]).
where the angular brackets define an average over the canonical ensemble. $\hat{U}(\Gamma_N; t)$ satisfies the Liouville equation and has the properties

$$\langle \hat{U} \rangle = 0; \quad \langle \hat{U}^2 \rangle = 1$$

leading to the initial conditions

$$\psi(0) = 1; \quad \dot{\psi}(0) = 0$$

It is then found that the time evolution equation for $\psi(t)$ reads

$$\dot{\psi}(t) = -\int_0^t K(\tau) \psi(t - \tau) \, d\tau$$

(a non-Markovian equation previously obtained by Zwanzig [53]) where the kernel $K(t)$ is related to the memory of the system and is defined through its Laplace transform by

$$K(s) = \hat{\phi}(s)[1 - (1/s) \hat{\phi}(s)]^{-1}$$

with $\hat{\phi}(s)$ the Laplace transform of the generalized force autocorrelation function

$$\phi(t) = \langle \hat{U}(\Gamma_N; 0) \hat{U}(\Gamma_N; t) \rangle$$

Berne et al. concluded from their analysis of the momentum autocorrelation function [which is the above expression, $\psi(t)$, with $U$ replaced by $p$] that the memory function $K(t)$ plays a sufficiently important role in the dynamical evolution of a system that it would be valuable to reformulate the representation of the transport coefficients in terms of $K(t)$. An analysis has been carried through [52] starting from the Kubo [Eqs. (33)] definitions of the transport coefficients. The following general expressions are obtained for any classical linear transport coefficient (at zero frequency)

$$\alpha = \left[ \lim_{s \to 0} \frac{\hat{\phi}(s)}{1 - (1/s) \hat{\phi}(s)} \right]^{-1}$$

with

$$\hat{\phi}(s) = \left\langle i \mathcal{L} \left[ \frac{1}{s - i \mathcal{L}} \right] \mathcal{L} \right\rangle$$

where $J$ is the normalized flux of the suitable momentum corresponding to the transport property considered, and $[s - i \mathcal{L}]^{-1}$ is the resolvent operator. This operator can be expanded into an infinite perturbation series and to the lowest order yields the following well-known result for weakly coupled systems:

$$\alpha^{-1} = \int_0^\infty dt \langle 0 | \mathcal{E}(t) \exp(i \mathcal{L}_0 t) J(0) \rangle_0$$
where $\mathcal{L}_0$ is the unperturbed Liouville operator, and $\langle \rangle_0$ means the average taken over the unperturbed Hamiltonian.

Similarly, in the case of the Brownian motion of a heavy particle, BBR retrieve the result of Lebowitz and Rubin [22] and Résibois and Davis [23] (see Section 2.3.2.). For strongly interacting systems (i.e., for simple liquids), the linear trajectory method first used by Helfand [54] has been generalized (and partly justified on a more formal basis) to yield the following results for systems subject to hard core repulsive forces and long (but finite) range soft attractive forces:

(a) Friction coefficient*:

$$\zeta_{LT} = -\frac{\rho}{3} \left(\frac{1}{2\pi}\right)^3 \int_0^\infty dt \int dk k^3 \exp[-(k^2\ell^2/2\rho)] \hat{V}(k) \hat{G}(k) \tag{36a}$$

with $\rho$ the number density, and $\hat{V}(k)$ and $\hat{G}(k)$ the Fourier transforms of the potential energy and of $[g^{(2)}(R) - 1]$.

(b) Reciprocal bulk viscosity coefficient:†

$$\phi_{LT}^{-1} = \frac{\rho kT}{3} \left(\frac{2}{\rho V}\right)^2 \frac{2}{3} \frac{\partial PV}{\partial V} - \frac{\rho kT}{3} \frac{\partial PV}{\partial V} + \frac{2\pi}{9} \rho^2 \int_0^\infty dR g^{(2)}(R) \frac{d}{dR} \left(\frac{du(R)}{dR}\right) \tag{36b}$$

with

$$A = \frac{\partial u(R)}{\partial R^e}, \quad \text{and} \quad B = R_t^e \left(\frac{\partial^2 u(R)}{\partial R^e \partial R^e}\right)$$

(c) Reciprocal shear viscosity coefficient:†

$$\eta_{LT}^{-1} = \int_0^\infty dt \left[\frac{2m}{\rho V} \left(\frac{2m}{\rho V}\right)^2 \left[1 + \frac{2\pi}{15} \frac{\rho kT}{\partial V} \int_0^\infty dR g^{(2)}(R) \frac{d}{dR} \left(\frac{du(R)}{dR}\right) \right] \right. \tag{36c}$$

* See Helfand [54].
† See Boon et al. [52].
288  STUART A. RICE, JEAN PIERRE BOON, AND H. TED DAVIS

with

\[ C = \frac{\partial u(R)}{\partial R^y} + R^y \frac{\partial^2 u(R)}{\partial (R^x)^2} \]

\[ D = \frac{\partial u(R)}{\partial R^x} + R^x \frac{\partial^2 u(R)}{\partial R^x \partial R^y} \]

\[ E = R^y \frac{\partial^2 u(R)}{\partial R^x \partial R^y} \]

No comparison with experimental data has yet been performed. Furthermore, it has been shown how the BBR treatment can be extended to the case of the frequency dependent transport phenomena [52]. In general, a transport coefficient reads

\[ \alpha(\omega) = \int_0^\infty dt \cos \omega t \psi(t) - i \int_0^\infty dt \sin \omega t \psi(t) \]

where the second term represents the nondissipative part of the coefficient. More explicitly, one obtains from the BBR analysis

\[ [\alpha(\omega)]^{-1} = i\omega + \frac{i\omega \Phi(\omega)}{i\omega - \Phi(\omega)} \]

with

\[ \Phi(\omega) = \langle \hat{U}(0) \frac{1}{i\omega - i\mathcal{L}} \hat{U}(0) \rangle \]

wherefrom in the high frequency limit, one finds

\[ [\alpha(\omega)]^{-1} = i\omega + \frac{\langle \hat{U}(\Gamma_N ; 0) \hat{U}(\Gamma_N ; 0) \rangle}{(i\omega)} + \mathcal{O}\left[ \frac{1}{(i\omega)^2} \right] + \ldots \]

a result which is equivalent to that of Zwanzig and Mountain [55]. It is obvious that in the limit of very high (or infinite) frequencies, the phenomenon is a truly nondissipative process. It would of course be of great interest to investigate this almost unknown domain in the field of transport phenomena (including the intermediate frequency region where both dissipative and nondissipative processes contribute), but the frequency range required for observing such phenomena in simple liquids is of the order of magnitude corresponding to the characteristic relaxation times of these fluids. It is expected that, thanks to the development of the laser technique, such experiments will be undertaken in the near future.
2.4. Phenomenological Analyses

By a phenomenological analysis we mean a correlation between sets of transport coefficients based on the principle of corresponding states. Principles of corresponding states have long been known and used to correlate both the equilibrium and transport properties of pure materials [56]. One means of derivation proceeds by dimensional analysis with either the critical constants or appropriate combinations of molecular parameters commonly used for the reduction of variables. Pitzer [57] has detailed a set of assumptions that allows the partition function to be cast into a reduced variable form, thus providing a statistical mechanical proof of the law of corresponding states for thermostatic properties. In essence, it is required that the intermolecular pair potential of all molecules be of the form $u = \varepsilon u^*(R/\sigma)$ where $\varepsilon$ and $\sigma$ are characteristic energy and distance constants and $u^*$ is a universal function of the one variable $R/\sigma$. Thus, the simple law of corresponding states may be expected to hold for spherical nonpolar molecules if, for instance, the potential is of the Lennard-Jones 6-12 type. Introduction of additional parameters such as a reduced dipole moment, the reduced de Broglie wavelength, or the reduced moment of inertia, into the equation of state extends the validity of the principle of corresponding states, although this sometimes limits its utility.

Pitzer originally limited consideration to systems whose translational degrees of freedom are classical and internal degrees of freedom are unexcited. The restriction to a classical description of translational motion may be removed by introducing a de Broglie wavelength as a parameter, leading to a mass dependence of the thermodynamic properties [58]. In addition to providing the basis for extension of the law of corresponding states to nonspherical potentials and quantum systems, the Pitzer technique of reducing the partition function has also been useful in deriving other expressions suitable to the description of mixtures, of molten salts, etc.

It is possible to show that with the intermolecular potential of the form suggested by Pitzer, a law of corresponding states can be derived for the transport coefficients. The demonstration will be based on the use of expressions for the transport coefficients in terms of time integrals of appropriate autocorrelation functions. These exact relationships were discussed in Section 2.3 (see also, Kubo et al. [59], Mori [60]).

The important point in our proof of the law of corresponding states will be that in addition to the distribution function, the solution of the mechanical equations of motion may be written in reduced variables. The principles are demonstrated for the shear viscosity in the quantum
mechanical case. The classical results, of course, follow in the limit \( \hbar \to 0 \). The bulk viscosity, thermal conductivity, and self-diffusion constant will be briefly discussed and the results stated.

The shear viscosity is given by the formula

\[
\eta = \frac{1}{V \text{Tr}(\exp[-H/kT])} \int_0^\infty \, dt \int_0^{1/kT} \, d\lambda \int \mathcal{D}p \, \exp[i(t + i\lambda/2\pi)2\pi H/\hbar] \\
\times \exp(-\lambda^2/4) \exp(-H/kT)
\]

(37)

Consider the reduced variables

Distance: \( R^* = R/\sigma \)

Mass: \( m^* = m/m = 1 \)

Pair potential: \( u^*(R^*) = u/\epsilon \)

From this basic set we find the reduced quantities

Temperature: \( T^* = Tk/\epsilon \)

Time: \( t^* = \epsilon^{1/2}m^{1/2}/\sigma \)

Momentum: \( p_i^* = p_i\sigma^{1/2}/\epsilon^{1/2} \)

Volume: \( V^* = V/\sigma^3 \)

Pressure: \( p^* = p\sigma^3/\epsilon \)

Planck constant: \( \hbar^* = \hbar/\sigma m^{1/2}/\epsilon^{1/2} \)

\( J_p \) tensor:

\[ J_p^* = J_p/\epsilon = \sum_i (p_i^* p_i^* + r_i^* F_i^*) - p^* V^* \]

(40)

(where \( F_i \) is the force on \( i \)), and the Hamiltonian takes the form

\[
H^* = H/\epsilon = \sum_i \left[ \frac{1}{2}(p_i^*)^2 + \sum_j u^*(R_{ij}^*) \right]
\]

The reduced Hamiltonian is a universal function of the momentum and position operators, so that for any particular reduced volume (which enters through the boundary conditions) there is a universal set of reduced eigenfunctions and energy levels.

The use of Eqs. (38) to (40) in Eq. (37) results in the reduction

\[
\eta^* = \eta_0^2(m\epsilon)^{-1/2}
\]

(41)

where \( \eta^* \) is given by Eq. (37) with a reduced variable replacing each unreduced variable. It is easily seen, for instance, that in an energy
diagonal representation the reduced viscosity is a universal function of reduced temperature, pressure, and Planck’s constant; i.e.,
\[ \eta^* = \eta^*(T^*, p^*, \hbar^*) \]  
(42)

where use has been made of the correspondence equation of state,
\[ V^* = V^*(T^*, p^*, \hbar^*) \].

It is pertinent to note that: (a) the density matrix has the reduced form \( \exp[-\hbar^*/r^*]/rr\{\exp[-\hbar^*/r^*]} \), and (b) the similarity transform with reduced unitary operator \( \exp[-i(t^* + i\hbar^*\lambda^*)] \) formally represents a reduced solution of the equations of motion, albeit in complex time.

The bulk viscosity differs from Eq. (37) only in involving diagonal elements of the tensor \( \mathbf{J}_p \). The correct reduction therefore is also
\[ \phi^* = \phi\sigma^2(m)^{-1/2} \]  
(43)

The representation of corresponding states for thermal conductivity follows in a manner completely paralleling the above, from the formula given, e.g., by Mori [60]. We find the appropriate reduction to be
\[ \kappa^* = \kappa^2m^{1/2}\epsilon^{-1/2}\sigma^{-1} \]  
(44)

Strictly speaking, self-diffusion is defined only in a classical system. One may, however, regard it as the mutual diffusion of a tagged species in a host fluid of identical molecules; in such a case a quantum mechanical formula similar to Eq. (37) may be used. Alternatively, from the start one may use the Einstein equation written in terms of a time integral of the momentum autocorrelation function. The operator that replaces the similarity transform, as a formal solution of the equations of mechanics, is \( \exp(it\mathcal{L}) \), where \( \mathcal{L} \) is the self-adjoint Liouville operator [54]. Using the previous reduction scheme one can easily show that the reduced classical coefficient of self-diffusion is
\[ D^* = Dm^{1/2}\epsilon^{-1/2}\sigma^{-1} \]  
(45)

An alternative formal demonstration* of the principle of corresponding states is also straightforwardly obtained from the Prigogine theory of irreversible processes (see Section 2.3) [61].

Consider the general form of the Boltzmann equation in the absence of external forces. This is
\[ \frac{\partial}{\partial t} f^{(N)} + \frac{\mathbf{p}}{m} \cdot \nabla f^{(N)} = \rho \int_0^t G(\tau) f^{(N)}(t - \tau) \, d\tau \]  
(46)

* This proof is slightly more general because it is valid regardless of the time dependence of the phenomena considered, while the use of the autocorrelation formalism introduces an implicit restriction to the study of quasi stationary processes.
with \( \rho \) the concentration, and \( p/m \) the velocity. We shall write the collision operator in terms of its Laplace transform:

\[
G(\tau) = -\left(\frac{1}{2\pi}\right)^3 \int e^{-is\tau} \tilde{G}(s) \, ds
\]

(47)

In (47)

\[
\tilde{G}(s) = \sum_{n=0}^{\infty} \lambda^n \tilde{G}^{(n)}(s)
\]

(48)

and

\[
\lambda^n \tilde{G}^{(n)}(s) = (-\lambda)^n \left\langle 0 \left| \delta L \left( \frac{1}{L_0 - \frac{1}{x}} \delta L \right)^{n-1} \right| 0 \right\rangle_{\text{irr}}
\]

(49)

By introduction of the reduced variables (38) and (39), the operator \( G(\tau) \) can be rewritten in the form:

\[
G(\tau) = e^{1/2m - 1/2} \sigma^2 G^*(p^*/m; \tau^*)
\]

(50)

where \( G^*(p^*/m; \tau^*) \) is a function of the reduced velocity and the reduced time variable.

When the "generalized" Boltzmann equation is developed according to Enskog's scheme, the first-order term leads to the following result when expressed in reduced variables:

\[
\rho f^{(0)} = \frac{(me)^{3/2}}{(2\pi)^{3/2}} \left(\frac{1}{T^*}\right)^{5/2} \exp \left[-\frac{(p - m\mu)^2}{2mkT}\right] p^* p^* : \nabla u
\]

(51)

Consider, for instance, the case of the shear viscosity. The preceding result, formally divided by the operator \( G^*(p^*/m) \), is introduced into the expression for the flux of momentum:

\[
J_p = (\rho/m) \int pp f^{(N)} \, dp
\]

(52)

By comparison with (2) Eq. (41) is retrieved with \( \eta^* \) a function of \( T^* \) only; \( \eta^* \) has the form

\[
\left(\frac{1}{2\pi}\right)^{3/2} \left(\frac{1}{T^*}\right)^{5/2} \int \exp\left[-\frac{[(p - m\mu)^2/2mkT]}{G^*(p^*/m)}\right] p^* d^3 p^*
\]

(53)

* One may show that the non-Markovian operator in (46) is then replaced by its Markovian limit \( G = \tilde{G}_{00} \) [see Eq. (32)].

† Expansion to higher order is straightforward: The collision operator is developed in the same way and the result is obviously equivalent to the first-order expression, as far as the variable reduction is concerned, since the concentration appears with the same powers in (51) and (52).
For liquids, which by the previous considerations may be expected to have transport properties obeying the simple law of corresponding states, the available data are discussed in a later section. It is found that deviations from corresponding states are larger than in the case of most equilibrium properties because of the sensitivity of interaction cross sections to the details of the potential form, which certainly differ among the members of the group monatomic, diatomic, and polyatomic molecules.

2.5. TRANSPORT PROPERTIES OF LIQUID MIXTURES

The study of transport phenomena in liquid mixtures has, unfortunately, been largely confined to systems with complex polyatomic molecules. As of this date, there are few data available for systems such as Ar-Kr, and only a small amount of data for systems such as N₂-O₂. Indeed, except for one investigation of the thermal conductivity of the liquid N₂-O₂ system, all other available data refer to the shear viscosities of liquid mixtures. Given the difficulties encountered in the formulation of the theory of transport in a one-component liquid, it is clear that more extensive experimental study has an important role to play in guiding the development of, and testing of, a theory of transport for liquid mixtures.

As usual, the earliest attempts at interpretation of the properties of liquid mixtures used many empirical parameters, simple model expressions, etc. [62]. Although these formulations still have utility in some engineering problems, they do not improve our understanding of the basic processes involved in transport phenomena in liquids and are therefore omitted from this review.

The extant theories of transport in liquid mixtures are conveniently classified as follows:

(a) The Eyring theory, based on the theory of absolute reaction rates [63];

(b) the Bearman-Kirkwood theory, based on the extension to multicomponent systems of the ideas of quasi-Brownian motion as developed in the Kirkwood theory of transport in pure liquids [64–66];

(c) the Rice-Allnatt theory, an approximate theory based on the extension to multicomponent systems of an approximate "small step diffusion" theory of transport in pure liquids developed by Rice and Kirkwood [67] and Rice and Allnatt [68];

(d) the Sedgwick-Collins theory [69], based on the extension to multicomponent systems of the theory of Collins and Raffel [70];
(e) the Wei-Davis extension to multicomponent systems of the kinetic
theory of Rice and Allnatt [71-73];
(f) the corresponding states theory [74]; and
(g) the McLaughlin-Davis theory [88] of mixtures of fluids composed
of particles interacting via the square-well potential.

The theories to be examined all refer to the case of a mixture of
monatomic molecules, thereby restricting the class of real systems
treated to Ar-Kr and similar mixtures. The extension of the theory to
include the internal degrees of freedom is difficult and has not yet been
accomplished even in the lowest order of approximation. Thus, despite
the knowledge that the collision dynamics and certain aspects of the
mechanisms of energy and momentum exchange are sensitive to the
form of the intermolecular potential and to the coupling between the
internal degrees of freedom and the translational motion, we are forced
to analyze the scanty available experimental data in terms of an "effective
potential" and similar concepts.

In this section we focus attention on the viscosity of a liquid mixture,
since it is this transport coefficient which has been most extensively
measured for simple liquid mixtures. Mutual diffusion coefficients and
the coefficients of thermal conductivity for simple liquid mixtures are
generally unavailable.

Since the main goal of this review—as has already been mentioned—is
to test the extant theories with respect to the existing experimental data,
we will omit the details of the theoretical developments and restrict
ourselves to the discussion of the several formal expressions for the
transport coefficients and the assumptions on which these results are
based. Nevertheless, for the convenience of the experimentalist interested
in this field, we also display the detailed relations as used for numerical
calculations.

2.5.1. The Eyring Theory*

The activated state theory of the viscosity of a liquid mixture is based
on the principles discussed in Section 2.1. This theory is, therefore,
subject to the criticisms already raised. Nevertheless, though we believe
the activated state theory to be fundamentally unsatisfactory, it cannot
be denied that the model is easily visualized and formalized with simple

* The reader should note that all the molecular theories cited [(b), (c), and (d)] also
use the theorem of corresponding states to reduce formulas to practical forms. In principle,
this is not necessary if sufficient information about the system is available, but in practice
the available information is always inadequate.
† See Glasstone et al. [63].
mathematics. Moreover, if the resulting formulas are considered to be parametric representations, then adjustment of the parameters often leads to useful representations of experimental data.

For the particular case of shear viscosity, the mechanism of momentum transfer is represented as a monomolecular process (reaction) with an intermediate slow step caused by passage through an activated state. That is, the shear stress leads to an environmental asymmetry whereby one quasi-lattice position is slightly lower in energy than an adjacent position (and higher than the opposite adjacent position). A molecule then passes from the higher energy to the lower energy site over a free energy barrier. The barrier involves free energy, rather than just energy, because of the necessity of moving many molecules to let one pass.

On this basis Eyring obtains the result [63] that the coefficient of shear viscosity of a pure liquid can be expressed in the form

$$\eta = \frac{N}{V} d^2 (2\pi m^2 kT)^{1/2} \exp \frac{-\Delta G^*}{kT}$$

In Eq. (54), $d^*$ is the width of the potential barrier, $m^*$ is the mass of the "activated particle," and $\Delta G^*$ is the free energy of activation.

Consider now a multicomponent system: If we assume that the displacements of the molecules of different species are independent, and that the viscosity is inversely proportional to the number of "jumps," the preceding expression can be straightforwardly generalized [74]. The result is an expression for the total fluidity as a sum of partial fluidities:

$$\varphi_M = \eta_M^{-1} = \sum \alpha \varphi_\alpha$$

The partial fluidity $\varphi_\alpha$ is evaluated, using the theorem of corresponding states, as a function of the fluidity of one of the pure components:

$$\varphi_\alpha(T_\alpha) = \varphi_\alpha \left( T_\alpha \frac{\epsilon_\alpha}{\epsilon_\alpha} \right) \times \frac{1/2 \sigma_\alpha^{1/2}}{\epsilon_\alpha^{1/2} \sigma_\alpha^{1/2}}$$

* A similar expression is found for the kinematic fluidity: $\Phi = \eta^{-1} \rho_m$ ($\rho_m$ = mass density) [74].

A double subscript refers to the pure component, while a single subscript refers to the component in the solution.

Given a particular form of the interaction potential, $\epsilon_\alpha$ and $\sigma_\alpha$ can be evaluated explicitly for a binary system (e.g., from the Prigogine molecular theory of solutions as applied to the Lennard-Jones potential).
For an ideal system, in which $e_{a\alpha}$ and $\sigma_{a\alpha}$ are the same for all components, Eq. (55) reduces to the weighted sum of the fluidities of the pure substances at the same temperature:

$$\Phi_{M}^{\text{ideal}} = \sum_{\alpha} x_{\alpha} \Phi_{a\alpha}$$  \hspace{1cm} (57)

Similar expressions are also easily obtained for the diffusion coefficient:

$$D_{a} = D_{a}^{0} \frac{d \ln a_{a}}{d \ln x_{a}}$$  \hspace{1cm} (58)

where $D_{a}^{0}$ is the diffusion coefficient of the species $a$ in an ideal solution, and $a_{a}$ is the activity of species $\alpha$. In the activated state theory, Eq. (58) can be transformed into:

$$\eta D_{a} = \frac{kT}{\delta} \frac{d \ln a_{a}}{d \ln x_{a}}$$  \hspace{1cm} (59)

with $\delta$ the lattice parameter of the quasi-crystalline medium (i.e., distance between two molecular layers). This expression has been extensively tested by Eyring and co-workers for a group of complex liquids, but is not of any assistance to us since no diffusion measurements have been carried out for simple liquid mixtures.

Finally, we merely note that an equivalent theoretical representation of the thermal conductivity of a multicomponent system is not possible using only the quasi-crystalline model and activated state theory, since this would require the existence of a universal relationship for the concentration dependence of the velocity of sound in liquid mixtures. This latter relationship is not known, and there is very little reason to believe that a simple relationship exists.

2.5.2. The Rice-Allnatt "Small Step" Theory of Mixtures (RASSD)*

In this section we discuss an approximate theory of transport in liquid mixtures, based on the hypothesis that the average diffusive displacement of a molecule in a dense fluid is small relative to the average intermolecular spacing. Although also developed by Rice and Allnatt, this theory should not be confused with the Wei-Davis [71–73] extension of the kinetic theory of Rice and Allnatt RA [4] to multicomponent systems. To distinguish between these theories, we will refer to the approximate theory by the initials RASSD for Rice-Allnatt small step diffusion theory [68].

It is neither possible nor desirable to reproduce herein the detailed

* See Rice and Allnatt [68].
analysis which leads to expressions for the composition dependence of the transport coefficients. In the case of the RASSD theory, as well as the theory of Bearman, the logical connections can be discerned from the accompanying diagram. * We shall examine some of these logical connections later, when the several theories are compared with one another.

Consider, first, the three hypotheses on which the RASSD theory is based. These are:

(a) The gradient of the pair interaction potential between molecules at time \( t + s \) may be expanded in a Taylor series about the gradient at time \( t \), and terms of higher order than the second may be neglected.

It is difficult to assess the accuracy of this approximation with any certainty. Nevertheless, some intuitive notions, while not rigorous, are worth discussing. The reader should note that if the intermolecular potential is approximately harmonic over the average small displacement, then the third derivative of the potential with respect to displacement is approximately zero. Now, interpretation of the known diffusion coefficients of liquids, as well as the computer simulation calculations of Rahman [76], suggests that the average diffusive displacement is of the order of one-tenth of the average intermolecular separation. Over this range of separation a parabola is not an impossibly bad fit to the bottom of the Lennard-Jones potential. Then, because the displacement \( |\Delta \mathbf{R}(s)| \) is small and the parabola fit to the potential not bad, we conclude that the product \( |(\Delta \mathbf{R}(s))^2 \mathbf{V}^3 w| \) is small relative to the terms in the expansion that are retained.

It is now important to point out that if the potential is represented as having a hard core component, as in the RA kinetic theory [4], the expansion of the potential as described is invalid. Berne and Rice [77] have carried through the analysis for the case of a pure fluid in which the soft part of the intermolecular potential is treated as in (a), and the hard core portion is treated separately. The methods used are fundamentally the same as in the original Rice-Kirkwood analysis [67], and the results are also almost the same, because although the hard core portion of the potential is dominant in defining the local statistical geometry, the rate of dissipation of energy is dominated by the soft part of the intermolecular interaction. Although a similar analysis has not been carried through for the mixture, it seems likely that the conclusion drawn remains valid.

(b) The distribution function in pair space may be approximated as the product of the local equilibrium pair configuration space distribution function and the zeroth order distribution function in momentum space.

* See diagram on page 316.
This is undoubtedly the mildest of the assumptions in the RAASD theory. Indeed, both in the gaseous phase, and in the liquid phase as described by the RA kinetic theory [4], it is the zeroth order local equilibrium contributions to the stress tensor and the heat flux which are dominant. The problems connected with determining the singlet and pair distribution functions in a liquid have been discussed by Rice and Gray [20] (see also Section 2.2). There is no doubt that, despite the large role played by the local equilibrium contribution, the distribution function obtained from the kinetic theory represents a considerable conceptual refinement, especially insofar as cross effects between momentum space distortions and configuration space distortions are included in the contribution to the dissipation of momentum and energy.

(c) The diffusion tensor in pair space may be approximated as the direct sum of the (diagonal) diffusion tensors in singlet space.

This approximation is probably the least accurate of those made in the RASSD theory. Indeed, it is to (c) that Rice and Kirkwood [67] attribute most of the discrepancy between the computed and observed transport coefficients for the small step diffusion theory applied to the one component liquid. A crude estimate of the error involved in (c) has been made by Berne and Rice, [77] but no systematic improvement of (c) can be expected until the molecular pair dynamics is well enough understood to permit determination of the distance at which (c) becomes inaccurate. Assumption (c) is certainly valid at large pair separations, and equally certainly invalid at small pair separations, but what large and small mean quantitatively is not at present known. Since even the crude correction of Berne and Rice greatly complicates the analysis of the mixture, we are constrained to use (c) in our development.

We now examine the expressions obtained by Rice and Allnatt for the transport properties of a multicomponent system. We will first display the several formulas and then transform these expressions into practical forms which can be used for direct numerical evaluation of the transport coefficients.

(i) The stress tensor in Eq. (2) can be written as the sum of partial stress tensors,

\[ \sigma_v = \sum_a \sigma_{va} \]  

where

\[ \sigma_{va} = -p_a I + 2\eta_a [\epsilon - \frac{1}{3} \nabla \cdot u] + \phi_a \nabla \cdot u \]  

\[ (60) \]  

\[ (61) \]
and

\[
\eta_\alpha = \sum_\beta \frac{m_{a\beta}}{30} \left( \frac{1}{\zeta_{\alpha}} + \frac{1}{\zeta_{\beta}} \right) c_{\alpha} c_{\beta} \int R_{a\beta}^2 \left( u''_{a\beta} + 4 \frac{u'_{a\beta}}{R_{a\beta}} \right) g^{(2)}_{a\beta}(R_{a\beta}) \, d^3 R_{a\beta} \quad (62)
\]

\[
\phi_\alpha = \sum_\beta \frac{m_{a\beta}}{30} \left( \frac{1}{\zeta_{\alpha}} + \frac{1}{\zeta_{\beta}} \right) c_{\alpha} c_{\beta} \int R_{a\beta}^2 \left( u''_{a\beta} + \frac{u'_{a\beta}}{R_{a\beta}} \right) g^{(2)}_{a\beta}(R_{a\beta}) \, d^3 R_{a\beta} \quad (63)
\]

Note that in the limit of the one-component system, Eqs. (62) and (63) reduce to the corresponding formulas given by Rice and Kirkwood [67].

Consider now the shear viscosity of a binary mixture:

\[
\eta_M = \frac{1}{2} \sum_\alpha \sum_\beta \frac{v_{\alpha} v_{\beta}}{V^2} \eta_{a\beta} ; \quad \alpha, \beta = 1, 2 \quad (64)
\]

\[
\eta_{a\beta} = \frac{1}{30} \frac{m_{a\beta}}{kT} \frac{N_a N_\beta}{v_{\alpha} v_{\beta}} (D_\alpha + D_\beta) \int R_{a\beta}^3 \left( u''_{a\beta} + 4 \frac{u'_{a\beta}}{R_{a\beta}} \right) g^{(2)}_{a\beta}(R_{a\beta}) \, d^3 R_{a\beta} \quad (65)
\]

If the Lennard-Jones potential is selected as representative of the pair potential, the functions \( \eta_{a\beta} \) may be expressed in terms of a new set of functions defined by

\[
\frac{B^{(2\beta)}}{m(\sigma_{12})} = 4 \epsilon_{a\beta} \frac{N_a N_\beta}{v_{\alpha} v_{\beta}}^{1/2} \int \left( \frac{\sigma_{a\beta}}{R_{a\beta}} \right)^m g^{(2)}_{a\beta}(R_{a\beta}) \, d^3 R_{a\beta} \quad (66)
\]

to which the principle of corresponding states can be applied.

After use of the theorem of corresponding states, and with the reduced mass replaced by its definition

\[
m_{a\beta}^{-1} = m_a^{-1} + m_\beta^{-1} \quad (67)
\]

\( \eta_M \) assumes the form

\[
\eta_M = \eta_1 \left( \frac{v_1}{V} \right)^2 \left( 1 + \frac{x_1}{x_1} M_1 \right) + \eta_2 \left( \frac{v_2}{V} \right)^2 \left( 1 + \frac{x_2}{x_2} M_2 \right) \quad (68)
\]

with

\[
M_1 = \frac{2m_2}{m_1 + m_2} (1 + \delta)^{1/2} \left( \frac{2 + \rho}{2} \right)^3 \quad (69)
\]

\[
M_2 = \frac{2m_1}{m_1 + m_2} (1 + \delta)^{-1/2} \left( \frac{2 + \rho}{2(1 + \rho)} \right)^3 \quad (70)^*
\]

\[
1 + \delta = \frac{\sigma_{22}}{\epsilon_{11}} ; \quad 1 + \rho = \frac{\sigma_{12}}{\sigma_{11}}
\]

* In this calculation, use has been made of the following combining rules:

\[
\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2} ; \quad \sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})
\]
The final expression (68) is useful for numerical calculations, since the partial viscosities $\eta_\alpha$ can be estimated from the corresponding states formula:

$$\eta_\alpha(T_\alpha) = \eta_{\alpha x} \left( T_\alpha \frac{e_{\alpha x}}{e_\alpha} \right) \frac{\varepsilon_{\alpha x}^{1/2} \sigma_{\alpha x}^2}{e_{\alpha x}^{1/2} \sigma_\alpha^2}$$

(71)

The partial molar volumes $v_\alpha$, which also appear in Eq. (68), are directly obtainable from the experimental equation of state. The reader should note that the last application of the theorem of corresponding states was introduced in order to eliminate the explicit dependence of the viscosity on the mutual diffusion coefficients, since these are unknown for simple liquid mixtures.

(ii) A similar analysis can be carried to completion for the thermal conductivity of a mixture. The total heat flux is found to be

$$q_v = \sum_{\alpha=1}^{v} Q_\alpha j_\alpha - \frac{1}{3} \sum_{\alpha} \sum_{\beta} N_\alpha N_\beta D_{\alpha \beta} \int R_{\alpha \beta}^2 \nabla^2 u_{\alpha \beta}$$

$$\times \left[ \frac{\partial}{\partial T} \left( \frac{g^{(2)}_{\alpha \beta}(R_{\alpha \beta})}{V^2} \right) \right]_p d^3 R_{\alpha \beta} \nabla T$$

$$+ 2 \sum_{\alpha} \sum_{\beta} N_\alpha N_\beta D_{\alpha \beta} \left[ \frac{\partial}{\partial T} \left( \frac{h_{\alpha \beta}}{V^2} \right) \right]_p \nabla T$$

(72)

with

$$h_{\alpha \beta} = h_{\alpha x} = \frac{1}{2} \int \left[ u_{\alpha \beta} - \frac{R_{\alpha \beta} U_{\alpha \beta}}{3} \right] g^{(2)}_{\alpha \beta}(R_{\alpha \beta}) d^3 R_{\alpha \beta}$$

(73)

For a stationary state heat flux $j_\alpha = 0$: comparison of Eqs. (1) and (72) yields the following result for the thermal conductivity of a multicomponent system:

$$\kappa_M = \sum_{\alpha} \sum_{\beta} \frac{N_\alpha N_\beta}{V^2} D_{\alpha \beta} \mathcal{K}_{\alpha \beta}$$

(74)

$$\mathcal{K}_{\alpha \beta} = \int R_{\alpha 3}^2 \left[ \frac{u_{\alpha \beta}^x}{3} + \frac{u_{\alpha \beta}^y}{R_{\alpha \beta}} - \frac{u_{\alpha \beta}^z}{R_{\alpha \beta}^2} \right]$$

$$\times \left[ \left( \frac{\partial g^{(2)}_{\alpha \beta}(R_{\alpha \beta})}{\partial T} \right)_p - 2 \alpha^{E} g^{(2)}_{\alpha \beta}(R_{\alpha \beta}) \right] d^3 R_{\alpha \beta}$$

(75)

where $\alpha^{E}$ is the coefficient of thermal expansion of the fluid:

$$\alpha^{E} = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p, x}$$

(76)
To reduce the thermal conductivity to dimensionless form we write (see Section 2.4)

$$K_{ab} = K_{a}^{b} \mathcal{K}_{ab}^{*}(T_{ab}^{*})$$

(77)

Now, rewriting (74) for a binary mixture,

$$\kappa_{M} = \sum_{\alpha} \sum_{\beta} \frac{\nu_{\alpha} \nu_{\beta}}{V_{2}} \kappa_{\alpha \beta} ; \quad \alpha, \beta = 1, 2$$

(78)

$$\kappa_{\alpha \beta} = \frac{N_{\alpha} N_{\beta}}{\nu_{\alpha} \nu_{\beta}} D_{\alpha}^{\beta} \mathcal{K}_{ab}^{*}$$

(79)

and introducing (77) into (79) together with use of the theorem of corresponding states, we finally obtain

$$\kappa_{M} = \kappa_{1} \left( \frac{\nu_{1}}{V} \right)^{2} \left[ 1 + \frac{x_{2}}{x_{1}} \left( \frac{2 + \rho}{2} \right)^{3} \right] + \kappa_{2} \left( \frac{\nu_{2}}{V} \right)^{2} \left[ 1 + \frac{x_{1}}{x_{2}} \left( \frac{2 + \rho}{2(1 + \rho)} \right)^{3} \right]$$

(80)

where the partial thermal conductivities $\kappa_{1}$ and $\kappa_{2}$ can be evaluated from the corresponding thermal conductivities of the pure components:

$$\kappa_{1}(T) = \kappa_{11} \left( \frac{T}{(1 + \delta)^{1/2}} \right) \frac{\sigma_{11}^{1/2}}{\epsilon_{11}^{1/2}}$$

$$\kappa_{2}(T) = \kappa_{22}(T(1 + \delta)^{1/2}) \frac{\sigma_{22}^{1/2}}{\epsilon_{22}^{1/2}}$$

(81)

A comparison of Eqs. (68) and (80) shows that the expression for the thermal conductivity of a mixture, in contrast with the equivalent expression for the viscosity of a mixture, contains no mass dependence. The fact that a mass difference between the components of a system has no influence on the thermal conductivity of that system should be subjected to experimental verification. At present, there are no data with which this prediction may be compared. Furthermore, the reader should note that the evaluations of the partial quantities (71) and (81) differ slightly in that a supplementary temperature dependence appears in the thermal conductivity through the function $\mathcal{K}^{*}(T_{ab}^{*})$, while $B_{m}^{(a \beta)}$ is almost independent of the temperature at constant volume. For an ideal mixture, both expressions (68) and (80) become simple linear forms:

$$\eta_{M}^{\text{Ideal}} = \sum_{\alpha} x_{\alpha} \eta_{\alpha \alpha}$$

(82)

$$\kappa_{M}^{\text{Ideal}} = \sum_{\alpha} x_{\alpha} \kappa_{\alpha \alpha}$$

(83)
Note that for the viscosity the definition of ideality given also requires that the components have equal mass.

(iii) In a binary system, the isothermal interdiffusion coefficient defined by

$$J_2 = -D_{21} \nabla c_2 = c_2(u_2 - u_1)$$

is found to be

$$D_{21} = \frac{kT[1 + (\ln \gamma_3/\ln c_2)_{T,p}]}{c_1 m_{12} A_{21}(\zeta_1^{-1} + \zeta_2^{-1})}$$

with

$$\gamma_x = -\sum_{\beta=1,2} \frac{c_\beta v_\beta^2 T}{3} \int R_{\alpha\beta} \left[ \frac{\partial}{\partial T} \left( \frac{g^{(2)}_{\alpha\beta}(R_{\alpha\beta})}{V^2} \right) \right] d^3R_{\alpha\beta}$$

$$A_{\alpha\beta} = \frac{1}{3} \int \nabla^2 u_{\alpha\beta} g^{(2)}_{\alpha\beta}(R_{\alpha\beta}) d^3R_{\alpha\beta}$$

Correspondingly, the self-diffusion coefficient $D_2 = kT/\zeta_2$ can be written as

$$D_2 = \frac{kT}{c_1 m_{12} A_{12}(\zeta_1^{-1} + \zeta_2^{-1}) + c_2 m_{22} A_{22}\zeta_2^{-1}}$$

For the case of isotopic diffusion, for which $\Lambda_{11} = \Lambda_{22} = \Lambda_{12}$, we have, therefore,

$$D_{21}/D_2 = 1 + [m_2 c_{21} \zeta_1 / m_{12} c_1 (\zeta_1 + \zeta_2)]$$

The coefficients of self-diffusion $D_1$ and $D_2$ are the coefficients measured by a tracer diffusion experiment at the given concentration; the coefficient of mutual diffusion $D_{21}$ is defined in Eq. (84).

(iv) The thermal diffusion factor for a binary mixture is defined by the relation

$$\nabla x_1 - a x_1 x_2 \nabla \ln T = 0$$

In the steady state the flux equation gives

$$\nabla T \mu_1 + R_{10} \nabla \ln T = 0$$

with

$$R_{10} = \gamma_1 + kT$$

and $\gamma_1$ defined by Eq. (86).
In the absence of a pressure gradient we also have
\[ \nabla T^{\mu_1} = \left( \frac{\partial \mu_1}{\partial x_1} \right)_{T,p} \nabla x_1 - \left( \frac{v_1 \alpha^E}{\beta} \right) \nabla \ln T \]

\[ \alpha^E = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p,x_1} ; \quad \beta = - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,x_1} \]  

On combining Eqs. (90)–(92) the thermal diffusion factor is found to be
\[ \alpha = \frac{(v_1 \alpha^E T/\beta) - R_{10}}{x_0} kT \left[ 1 + \frac{\partial \ln f_3}{\partial \ln x_2}_{T,p} \right] \] (93)

and
\[ R_{10} = \frac{2}{c_1} \left( \frac{\partial p_1}{\partial \ln T} \right)_{c_1,c_2,p} - kT \]

2.5.3. The Theory of Collins and Raffel*

Perhaps the most important difference between the Rice-Kirkwood development and the Collins and Raffel theory lies in the method of introducing the element of irreversibility. Whereas Rice and Kirkwood use the hypothesis of time smoothing, Collins and Raffel use a special subensemble average to introduce a friction coefficient [70]. The average is performed in the following way. The mean behavior of a physical system is represented by the average behavior of a subassembly constructed from \( \mathcal{N} \)-replica systems. The subassembly velocity is defined by
\[ \left\langle \frac{\mathbf{p}_1}{m} \right\rangle = \frac{1}{\mathcal{N}} \sum_{\mu=1}^{\mathcal{N}} \frac{\mathbf{p}_{1\mu}}{m} \quad \text{at} \quad t_0 \leq t \] (94)

where \( \mathbf{p}_{1\mu}/m \) is the velocity of a given molecule in the \( \mu \)th replica. The average force acting on the central molecule is then expressed in the same form as used by Rice and Kirkwood. However, in place of time smoothing, it is the time derivative of the force which is used to introduce the element of irreversibility in the corresponding statistical mechanical ensemble. In more detail, Collins and Raffel make the ansatz:
\[ \left\langle \frac{d \mathbf{F}_1}{dt} \right\rangle_{t_0} = - \frac{\zeta}{m} \left\langle \frac{d \mathbf{p}_1}{dt} \right\rangle_{t_0} \] (95)

Combination of Eq. (95) with Newton’s second law then yields
\[ \left\langle \frac{d \mathbf{F}_1}{dt} \right\rangle_{t_0} = \frac{\zeta^2}{m^2} \mathbf{p}_1^0 \] (96)

* Referred to hereafter as CR. See Sedgwick and Collins [69], and Collins and Raffel [70].
The average in this expression is evaluated by means of a perturbation calculation, with the supplementary assumption that the deviations from the equilibrium form of the radial distribution function may be neglected. The result for $\zeta^2$ is then identical with the expression found by Rice and Kirkwood [67].

The derivation of the other transport coefficient is based upon a similar argument. The rate a transport of the dynamical variable $A$ across the bounding surface $S$ of a closed domain is given in terms of the generalized stress $\Sigma$ on the surface,

$$\Sigma = -\alpha \frac{\partial A}{\partial R} \cdot n$$

(97)

with $n$ the normal to the surface and $\alpha$ the transport coefficient corresponding to the dynamical variable $A$. The evaluation of $\langle \Delta A \rangle$ and $\langle \Delta S \rangle$ follows from the definition of the generalized stress in the form

$$\Sigma = \frac{d}{dt} \frac{\partial \langle \Delta A \rangle}{\partial \langle \Delta S \rangle} \sim \frac{d}{dt} \left( \frac{\partial A}{\partial R} \cdot n \right)$$

(98)

Substitution of this result into the time derivative of $\Sigma$ leads to

$$\frac{d}{dt} \Sigma = -\alpha \frac{d}{dt} \left( \frac{\partial A}{\partial R} \cdot n \right)$$

(99)

When $\Sigma$ is chosen to correspond to the pressure tensor and the heat flux, and the indicated average performed, the following results are obtained for the transport coefficients by comparison with the hydrodynamic equations:

$$\eta^2 = \frac{0.510}{45} \frac{m}{V^2} V^{-1/3} \int R^2 \left( u'' + 3 \frac{u'}{R} \right) g^{(2)}_0(R) d^3R$$

$$\phi^2 = \frac{1.020}{27} \frac{m}{V^2} V^{-1/3} \int R^2 \left( u'' + 3 \frac{u'}{R} \right) g^{(2)}_0(R) d^3R$$

$$\kappa^2 = \frac{2.040}{9} \frac{kC_v}{V^2} V^{-1/3} \int R^2 \left[ \frac{u'}{R} + \alpha T \left( u'' + 3 \frac{u'}{R} \right) \right] g^{(2)}_0(R) d^3R$$

(100)

* Referred to hereafter as RK.

† The form of this result is very important in the Collins and Raffel theory because it shows that the final results involve the squares of the transport coefficients.
with $C_v$ the specific heat at constant volume. The reader should note that despite the different approximations used by CR [70] and RK [67], these expressions are very similar in structure to those obtained by Rice and Kirkwood, though the latter are for the first powers of the coefficients. The generalization of the calculation of the shear viscosity to the case of mixtures follows in a straightforward manner, as shown by Sedgwick and Collins [69]. For a binary system it is found that

$$\frac{\eta_M}{x_1m_1 + x_2m_2} = \sum_\alpha \sum_\beta \left( \frac{v_\alpha v_\beta}{V} \right)^{7/3} \eta_{\alpha\beta}^2; \quad \alpha, \beta = 1, 2$$

$$\eta_{\alpha\beta}^2 = \frac{0.1735}{15} \frac{x_\alpha x_\beta}{(v_\alpha v_\beta)^{2/3}} \int R_{\alpha\beta}^2 \left( u_{\alpha\beta} + 4 \frac{u_{\alpha\beta}^3}{R_{\alpha\beta}^3} \right) g^{(2)}_{\alpha\beta} d^3 R_{\alpha\beta}$$

In order to make numerical calculations, it is convenient to introduce the same arguments as used in the preceding paragraph (principle of corresponding states and regular solution approximation). The following expressions are obtained:

$$\eta_M^2 = x_1^3 \eta_1^2 \left( \frac{v_1}{V} \right)^{7/3} \left( 1 + \frac{x_2 m_2}{x_1 m_1} \right) \left( 1 + \frac{x_1 M'_1}{x_2 M'_2} \right)$$

$$+ x_2^3 \eta_2^2 \left( \frac{v_2}{V} \right)^{7/3} \left( 1 + \frac{x_1 m_1}{x_2 m_2} \right) \left( 1 + \frac{x_1 M'_1}{x_2 M'_2} \right)$$

with

$$M'_1 = (1 + \delta)^{1/2} \left( \frac{2 + \rho}{2} \right)^3$$

$$M'_2 = (1 + \delta)^{-1/2} \left( \frac{2 + \rho}{2(1 + \rho)} \right)^3$$

Once again, there are great similarities in the structures of expressions (68) and (102). It should also be mentioned that the differences in the mass and composition dependences arise not only from the fact that the CR expression is for the square of the coefficient of shear viscosity, while the RASSD result is not, but also because in the generalization of the CR development the mass of the pure liquid is replaced by $(x_1 m_1 + x_2 m_2)$.

Several further approximations have been used by Sedgwick and Collins to transform the generalized expression (101) into practical forms, but these differ only slightly from each other and from Eq. (102).

2.5.4. The Theory of Bearman and Co-Workers*

Although the mathematical techniques employed by Bearman are

* Referred to hereafter as BJ. See work of Bearman and co-workers [64–66].
quite different from those used in the RASSD theory, the spirit of the
two calculations is similar in that they both are based on Kirkwood’s
pioneer work [5].

The main assumption introduced by Bearman and Jones [66] in
their extension of the Kirkwood theory to the case of liquid mixtures
is found in the form of the generalization of the expression for the mean
force acting on a given molecule in a pure medium:

$$ F_{a,i}^{(1,1)} = -\sum_{\beta} \zeta_{a \beta} \left( \frac{p_a}{m_a} - \frac{p_\beta}{m_\beta} \right) $$

The generalization of this expression to the space of molecular pairs is
much like the third assumption used in the RASSD theory. The mean
frictional force $F_{a \beta}^{(2,1)}$ in the configuration space of molecular pairs
is defined by the six-dimensional sum $F_{a \beta,1}^{(2)} \oplus F_{a \beta,2}^{(2)}$, and is linearly
related to the pair space velocity through the same friction coefficients
that appear in $F_{a}^{(1,1)}$ and $F_{\beta}^{(1,1)}$

$$ F_{a \beta}^{(2,1)} = -\frac{1}{2} \sum_{\gamma \delta} \zeta_{a \beta, \gamma \delta} \cdot \left[ \frac{p_{a \delta}}{m_{a \delta}} - \left( \frac{p_{\gamma}}{m_{\gamma}} \oplus \frac{p_{\delta}}{m_{\delta}} \right) \right] $$

with

$$ \frac{p_{a \delta}}{m_{a \delta}} = \frac{p_{a \beta,1}^{(2)}}{m_{a \beta}} \oplus \frac{p_{a \beta,2}^{(2)}}{m_{a \beta}} $$

and

$$ \zeta_{a \beta, \gamma \delta} = c_{\gamma} c_{\delta} 1_1 \oplus c_{\beta} 1_2 $$

Given the direct sum form of the friction tensor, direct calculation leads
to the following result for the coefficient of shear viscosity of a binary
system (note the similarity in structure to the RASSD expression):

$$ \eta_{\alpha \beta} = \sum_{\alpha} \sum_{\beta} \frac{v_{a \beta}}{V^2} \eta_{a \beta} ; \quad \alpha, \beta = 1, 2 $$

$$ \eta_{a \beta} = \frac{1}{30} N_{a \beta} N_{\alpha \beta} \frac{1}{D_a + D_\beta} \int R_{a \beta} u_{a \beta} \psi_{a \beta}^{*(2)} | \delta_{a \beta} (R_{a \beta}) | d^3 R_{a \beta} $$

(105a)

where $\psi_{a \beta}^{*(2)}$ is a perturbation function representing the distortion of the
pair distribution function in the fluid flow field (see also Section 2.2).
Equation (105a) reduces to the results of Kirkwood et al. [78] and
Zwanzig et al. [79], for a pure fluid when $\alpha = \beta$ or if $\alpha$ or $\beta = 0$. When
the assumption that the mixture may be described as a regular solution is introduced (the volumes are assumed additive and the radial distribution functions assumed composition independent) $\psi^{(2)}_{\alpha\beta}$ is a constant, and one obtains from (105a):

$$\eta_M = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12}$$

(105b)

$$\eta_{\alpha\beta} = \frac{1}{30} \frac{1}{V^2} \int R_{\alpha\beta} \mu'_{\alpha'\beta'} \psi^{(2)}_{\alpha'\beta'} (R_{\alpha'\beta'}) d^3 R_{\alpha'\beta'}$$

Once again it is seen that the principle of corresponding states is easily employed to obtain useful formulas for numerical evaluation of the coefficient of shear viscosity.

The reader should note that the RASSD and BJ results seemingly involve the friction coefficient in different ways. This difference is, however, only superficial, and Rice has shown how a peak approximation to the integrals for the viscosity renders the functional dependence of $\eta$ on $D$ the same in both theories [80]. The reader should also note the different ways in which the composition dependence of the viscosity enters the two theories.

2.5.5. The Wei-Davis Extension of the Rice-Allnatt Theory to Multicomponent Systems*

The starting equations of the Wei and Davis theory [71–73] are the multicomponent kinetic equations of the Rice-Allnatt model. However, their solutions of these equations differ in the following two respects from the corresponding solutions of Rice and Allnatt:

(a) The temperature $T$ appearing in the Fokker-Planck operator [Eqs. (6) and (15)] was identified by Wei and Davis as an effective kinetic temperature while Rice and Allnatt assumed $T$ to be the local equilibrium temperature. The consequences of identifying $T$ with an effective kinetic temperature are that the linearized RA equations then lead to an $H$-Theorem [73] and that the mass, momentum, and kinetic energy are solutions of the homogeneous linearized equations. The final formulas for the transport coefficients for a pure fluid are unchanged by the WD choice of $T$.

(b) In evaluating the doublet equation, Wei and Davis [72] used the chaos assumption

$$f^{(2)}(\mathbf{R} - \frac{1}{2}\mathbf{k}, \mathbf{p}_1; \mathbf{R} + \frac{1}{2}\mathbf{k}, \mathbf{p}_2; t)$$

$$= \delta^{(2)}(\mathbf{R}, \mathbf{0}) f^{(1)}(\mathbf{R} - \frac{1}{2}\mathbf{k}, \mathbf{p}_1; t) f^{(1)}(\mathbf{R} + \frac{1}{2}\mathbf{k}, \mathbf{p}_2; t)$$

* Hereafter referred to as WD. See Wei and Davis [71–73].
for two particles undergoing a binary hard core collision. This assumption turns out, *a posteriori*, to be equivalent to assuming that $G_2$, the net mean force on a particle at $R_i$ when another particle is at $R_j$, vanishes when $R_{ij} = \sigma$. On the other hand, Rice and Allnatt, in effect, used the assumption that $\phi^{(2)}(i, j)$, the perturbation to the doublet velocity distribution function, exhibits the following properties:

$$
\phi^{(2)}(i, j) = \phi^{(2)}(i) + \phi^{(2)}(j),
$$

$$
\phi^{(2)}(1, 2) + \phi^{(2)}(2, 3) + \phi^{(2)}(3, 1) = 2[\phi^{(2)}(1) + \sigma^{(2)}(2) + \phi^{(2)}(3)]
$$

Under the WD chaos assumption the soft interaction contribution to the transport coefficients, e.g., $\kappa_v (R > \sigma)$, involves the total friction coefficient $\zeta$, while under the RA division of $\phi^{(2)}(i, j)$ the same coefficients involve $\zeta_s$, the soft part of the friction coefficient. At present there is no *a priori* way to decide which assumption is better. In fact, as will be shown in Section 3, the results of Wei and Davis lead to better agreement of theory and experiment for viscosity while Rice and Allnatt’s results lead to better agreement of theory and experiment for thermal conductivity.

Other than the points mentioned, the details of the WD calculations for mixtures are quite similar to the RA calculations for pure fluids. The following is a summary of their results for a binary mixture:

(i) Shear viscosity

$$
\eta = \eta_K + \eta_v (R = \sigma) + \eta_v (R > \sigma)
$$

$$
\eta_K = \sum_{a=1}^{2} \frac{1}{2} \rho_a kT \zeta_a
$$

$$
\eta_v (R = \sigma) = \sum_{a, b=1}^{2} \frac{1}{2} \rho_a \rho_b \zeta_a \zeta_b
$$

$$
\eta_v (R > \sigma) = \sum_{a, b=1}^{2} \frac{2\pi}{5kT} \frac{\zeta_a \zeta_b}{\zeta_a + \zeta_b} \rho_a \rho_b \int_{a_b,0}^{(2)} g_{a_b,0}^{(2)} (R) R^3 \psi_{a_b}^{(2)} d\omega_{a_b} (R) dR
$$

where

$$
\sigma_{a_b} = (\sigma_a + \sigma_b)/2
$$

$$
M_a = m_a (m_1 + m_2)
$$

$$
\mu_{a_b} = m_a m_b (m_1 + m_2)
$$

$$
\theta_{a_b} = \frac{4\pi}{3} \frac{\rho_a \rho_b}{\rho_a + \rho_b} \sigma_{a_b} \delta_{a_b,0}(\sigma_{a_b})
$$
The quantity $\psi^{(2)}$ satisfies the same differential equation as Eq. (22) if $g_0^{(2)}$ is replaced by $g_0^{(2),0}$.

The other quantities appearing in Eq. (106) are defined by

\[
b_{11} = \frac{\beta_{(1)} b_{(-1-1)} - \beta_{(-1)} b_{(1-1)}}{b_{(1)} b_{(-1-1)} - b_{(-1)} b_{(1-1)}}
\]

\[
b_{1(-1)} = \frac{-\beta_{(1)} b_{(-1)} + \beta_{(-1)} b_{(1)}}{b_{(1)} b_{(-1-1)} - b_{(-1)} b_{(1-1)}}
\]

with the further definitions

\[
\beta_{(1)} = \frac{5}{\rho_2} \left( 1 + \frac{3}{6} \theta_{11} + \frac{3}{6} M_2 \frac{P}{\rho_1} \theta_{12} \right)
\]

\[
\beta_{(-1)} = \frac{5}{\rho_1} \left( 1 + \frac{3}{6} \theta_{22} + \frac{3}{6} M_1 \frac{P}{\rho_2} \theta_{22} \right)
\]

\[
b_{11} = \frac{5}{6} (5M_1 M_2 + 3M_2^2) \sigma_{12}^0 \left( \frac{2\pi k T}{\mu_{12}} \right)^{1/2} \mathcal{g}_{12,0}^{(2)}(\sigma_{12})
\]

\[
+ 8 \rho_1 \rho_2 \sigma_{11}^0 \left( \frac{\pi k T}{m_1} \right)^{1/2} \mathcal{g}_{11,0}^{(2)}(\sigma_{11}) = \frac{5}{m_1 \rho_2} (\rho_{1s}^{s} + \rho_{2s}^{s})
\]

\[
b_{(-1-1)} = \frac{5}{6} (5M_1 M_2 + 3M_2^2) \sigma_{22}^0 \left( \frac{2\pi k T}{\mu_{12}} \right)^{1/2} \mathcal{g}_{12,0}^{(2)}(\sigma_{12})
\]

\[
+ 8 \rho_1 \rho_2 \sigma_{22}^0 \left( \frac{\pi k T}{m_2} \right)^{1/2} \mathcal{g}_{22,0}^{(2)}(\sigma_{22}) = \frac{5}{m_2 \rho_1} (\rho_{1s}^{s} + \rho_{2s}^{s})
\]

\[
b_{(-1-1)} = -\frac{5}{6} M_1 M_2 \sigma_{12}^0 \left( \frac{2\pi k T}{\mu_{12}} \right)^{1/2} \mathcal{g}_{12,0}^{(2)}(\sigma_{12})
\]

and finally

\[
\zeta_s = \sum_{\beta=1}^{2} \rho_{\beta} \sigma_{\alpha\beta}^2 \mathcal{g}_{0}^{(2)}(\sigma_{\alpha\beta}) \left[ 2\pi \mu_{\alpha\beta} k T \right]^{1/2} + \sum_{\beta=1}^{2} \rho_{\beta} \sigma_{\alpha\beta}^2
\]

\[
\mathcal{g}_{0}^{(2)} = \frac{1}{3kT} \int_{0}^{r} \left( \mathbf{F}_{\alpha\beta}^{(S)}(\mathbf{R}) \cdot \mathbf{F}_{\alpha}^{(S)}(\mathbf{R}^{(N)}) + \frac{\varepsilon}{m} \mathbf{B}^{(N)} \right) ds
\]

(ii) Bulk viscosity

\[
\phi = \phi_{\sigma}(R = \sigma) + \phi_{\sigma}(R > \sigma)
\]
where

$$\phi_v (R = \sigma) = \sum_{\alpha, \beta=1}^{2} \frac{1}{2} (\rho_{\alpha} + \rho_{\beta}) \theta_{\alpha \beta} kT$$

$$\times \left\{ \left[ (-1)^{\mu_{\alpha}} \frac{M_{\beta}}{\rho_{\alpha}} + (-1)^{\mu_{\beta}} \frac{M_{\alpha}}{\rho_{\beta}} \right] l_{(\sigma)} \right. - \left. \frac{\zeta_{\alpha} \zeta_{\beta}}{\zeta_{\alpha}^2 + \zeta_{\beta}^2} \frac{\psi_{\alpha \beta}^{(0)} (R = \sigma)}{3kT} + \frac{2}{3} \left( \frac{2\mu_{\alpha} \sigma_{\alpha \beta}}{\pi kT} \right)^{1/2} \right\}$$

$$\phi_v (R > \sigma) = \sum_{\alpha, \beta=1}^{2} \frac{2\pi \rho_{\alpha} \rho_{\beta}}{3kT} \frac{\zeta_{\alpha} \zeta_{\beta}}{\zeta_{\alpha} + \zeta_{\beta}}$$

$$\times \int_{\sigma_{\alpha \beta}}^{\infty} g^{(0)}_{\alpha \beta, 0}(R) R^{3} \psi_{\alpha \beta}^{(0)}(R) \frac{d\mu_{\alpha \beta}}{dR} dR$$

where $\psi_{\alpha \beta}^{(0)}$ is determined from the differential equation

$$\frac{d}{dR} R^2 g^{(1)}_{\alpha \beta, 0}(R) \frac{d}{dR} \psi_{\alpha \beta}^{(0)}(R) - R^3 \frac{d}{dR} g^{(2)}_{\alpha \beta, 0}(R) + 3R^2 \left( \frac{\partial g^{(0)}_{\alpha \beta, 0}}{\partial \ln \rho} \right)_T = 0$$

with the boundary conditions

$$\psi_{\alpha \beta}^{(0)} = 0 \quad \text{for} \quad R \to \infty$$

$$\frac{d}{dR} \psi_{\alpha \beta}^{(0)} = 0 \quad \text{for} \quad R \to \sigma_{\alpha \beta}^+$$

The remaining quantity to be defined is

$$l_{(\sigma)} = \left[ \theta_{12} \left( M_1 \frac{\rho_2}{\rho_1} - M_2 \frac{\rho_1}{\rho_2} \right) + \theta_{22} - \theta_{11} \right] A^{-1}$$

with

$$A = \rho_1 \rho_2 \left[ 8M_1 M_2 \left( \frac{\rho}{\rho_1 \rho_2} \right)^2 \theta_{12} \left( \frac{2\pi kT}{\mu_{12}} \right)^{1/2} g^{(1)}_{12, 0}(\sigma_{12}) + \left( \frac{3\rho^2}{m_1 + m_2} \right) \frac{\rho_1 \rho_2}{\rho_1 \rho_2} \gamma_{12} \right]$$

(iii) Thermal conductivity

$$\kappa = \kappa_K + \kappa_v (R = \sigma) + \kappa_v (R > \sigma) \quad (108)$$

where

$$\kappa_K = - \sum_{\alpha=1}^{2} \frac{4}{5} \rho_{\alpha} k \left( \frac{2kT}{m_{\alpha}} \right)^{1/2} \left[ a_{\alpha(1)} - d_{\alpha(1)} \frac{a_{(0)}}{d_{(0)}} \right]$$
\[ \kappa_\nu (R = \sigma) = -\frac{2}{\alpha,\beta-1} \frac{\mu_\alpha M_\beta (\rho_\alpha + \rho_\beta) \theta_{\alpha\beta} k \left( \frac{2kT}{\mu_{\alpha\beta}} \right)^{1/2}} {M_\beta^{1/2} \left[ a_{\alpha(1)} - d_{\alpha(1)} \frac{a_{\alpha(0)}}{d_{\alpha(0)}} \right] + M_\alpha^{1/2} \left[ a_{\beta(1)} - d_{\beta(1)} \frac{a_{\beta(0)}}{d_{\beta(0)}} \right] - \frac{4 \sigma_{\alpha\beta}}{3 \sqrt{\pi}}} \]

\[ \kappa_\nu (R > \sigma) = \frac{2}{\alpha,\beta-1} \frac{\pi} {6 \rho_\alpha \rho_\beta kT} \left( \frac{\xi_\alpha + \xi_\beta} {\xi_\alpha \xi_\beta} \right) \]

\[ \times \int_{\sigma_{\alpha\beta}}^{\infty} g_{\beta,0}^{(q)} (R) R^2 \left\{ 3u_{\alpha\beta} (R) - R \frac{d}{dR} u_{\alpha\beta} (R) \right\} \frac{\partial}{\partial R} \ln g_{\alpha,0}^{(q)} (R) dR \]

with the definitions

\[ a_{1(1)} = (\alpha_{(1)} a_{(-1-1)} - \alpha_{(-1)} a_{(1-1)}) / (a_{(11)} a_{(-1-1)} - a_{(1-1)}) \]

\[ a_{2(1)} = (-\alpha_{(1)} a_{(-1-1)} + \alpha_{(-1)} a_{(1-1)}) / (a_{(11)} a_{(-1-1)} - a_{(1-1)}) \]

\[ d_{1(1)} = - (a_{(-1-1)} a_{(1-1)} - a_{(1-1)} a_{(-1-1)}) \delta_{(0)} / [a_{(00)}(a_{(11)} a_{(-1-1)} - a_{(1-1)})] \]

\[ d_{2(1)} = - (a_{(11)} a_{(1-1)} - a_{(1-1)} a_{(1-1)}) \delta_{(0)} / [a_{(00)}(a_{(11)} a_{(-1-1)} - a_{(1-1)})] \]

\[ d_{(0)} = \delta_{(0)} / a_{(00)} \]

\[ a_{(0)} = (\alpha_{(1)} d_{1(1)} + \alpha_{(-1)} d_{2(1)}) / \delta_{(0)} \]

\[ \delta_{(0)} = 3 \rho_2 (2kT)^{1/2}/(2 \rho_1 \rho_2) \]

\[ \alpha_{(1)} = - \frac{15}{4 \rho_2} \left( \frac{2kT}{m_1} \right)^{1/2} \left( 1 + \frac{3}{8} \theta_{11} + \frac{9}{8} M_1 M_2 \rho_1 \theta_{12} \right) \]

\[ \alpha_{(-1)} = - \frac{15}{4 \rho_1} \left( \frac{2kT}{m_2} \right)^{1/2} \left( 1 + \frac{3}{8} \theta_{22} + \frac{9}{8} M_1 M_2 \rho_2 \theta_{12} \right) \]

\[ a_{(00)} = 4 \sigma_{12}^2 (2 \pi \mu_{12} kT) \left( \frac{g_{11,0}^{(q)} (\sigma_{12})}{g_{11,0}^{(q)} (\sigma_{12})} + \frac{\sigma_{12}^2}{g_{12,0}^{(q)} (\sigma_{12})} \right) \]

\[ a_{(11)} = M_1 (30 M_1^2 + 13 M_2^2 + 16 M_1 M_2) \sigma_{12}^2 \left( \frac{2 \pi kT}{\mu_{12}} \right)^{1/2} \left( g_{11,0}^{(q)} (\sigma_{12}) \right) \]

\[ + 8 \frac{\rho_1 \sigma_{12}^2}{\rho_2} \left( \frac{\pi kT}{m_1} \right)^{1/2} g_{11,0}^{(q)} (\sigma_{12}) \]

\[ + \frac{45}{4 \rho_2 m_1} (p_{15}^S + p_{25}^S) \]

\[ a_{(-1-1)} = M_1 (30 M_1^2 + 13 M_2^2 + 16 M_1 M_2) \sigma_{12}^2 \left( \frac{2 \pi kT}{\mu_{12}} \right)^{1/2} \left( g_{11,0}^{(q)} (\sigma_{12}) \right) \]

\[ + 8 \frac{\rho_1 \sigma_{12}^2}{\rho_2} \left( \frac{\pi kT}{m_2} \right)^{1/2} g_{22,0}^{(q)} (\sigma_{22}) \]

\[ + \frac{45}{4 \rho_1 m_2} (p_{15}^S + p_{25}^S) \]
\[ a_{(1-1)} = a_{(-11)} = -27(M_1 M_2)^{3/2} \sigma_{12}^2 \left( \frac{2\pi kT}{\mu_{12}} \right)^{1/2} \delta_{12,0}(\sigma_{12}) \]
\[ a_{(10)} = a_{(01)} = -2M_2^{3/2} \sigma_{12}^2 (2\pi kT)^{1/2} \delta_{12,0}(\sigma_{12}) \]
\[ a_{(0-1)} = a_{(-10)} = 2M_1^{3/2} \sigma_{12}^2 (2\pi kT)^{1/2} \delta_{12,0}(\sigma_{12}) \]

(iv) Mutual diffusion

\[ D_{12} = \left( \frac{kT}{2} \right)^{1/2} \frac{\rho_1 \rho_2}{\rho^2} d_{(0)} \]  

(v) Thermal diffusion ratio

\[ k_T = \frac{a_{(0)}}{d_{(0)}} + \frac{1}{2} \theta_{12}(M_1 - M_2) \]

The above formulas for the mutual diffusion and thermal diffusion ratio refer to the following equation for the relative diffusion velocity \( u_2 - u_1 \):

\[ u_2 - u_1 = \frac{\rho^2}{\rho_1 \rho_2} D_{12}(d + k_T \nabla \ln T) \]

where the diffusion driving force \( d \) is given by

\[ d = \frac{m_1 m_2 \rho_1 \rho_2}{(m_1 \rho_1 + m_2 \rho_2) \rho} \left( \frac{1}{m_2} X_2 - \frac{1}{m_1} X_1 + \frac{1}{m_2} F_2^* - \frac{1}{m_1} F_1^* \right) \]

\[ + \frac{1}{m_1 \rho_1} \nabla \rho_1 kT \left( 1 + \theta_{11} + \frac{1}{2} \frac{\rho}{\rho_2} \theta_{12} \right) \]

\[ - \frac{1}{m_2 \rho_2} \nabla \rho_2 kT \left( 1 + \theta_{22} + \frac{1}{2} \frac{\rho}{\rho_1} \theta_{12} \right) \]

\[ + \frac{1}{2} \theta_{12} \nabla \ln \frac{\rho_2}{\rho_1} \]

where \( X_\alpha \) denotes the external force on particle \( \alpha \). Another choice of diffusion driving force must of course be accompanied by a corresponding change in the definition of \( D_{12} \) and/or \( k_T \).

The expressions for the viscosities and thermal conductivity can be reduced to one-component formulas by assuming that the mixture is an equimolar mixture of two identical species. In this case \( \rho_1 = \rho_2 = \rho/2 \), and all of the molecular parameters are identical, e.g., \( \sigma_{11} = \sigma_{12} = \sigma_{22} \), etc.

In the limit that the soft potentials all go to zero, the WD formulas reduce to the corresponding formulas for a mixture of hard spheres, the latter having been derived by Thorne [81] from Enskog's kinetic equation. Also, it should be noted that \( \eta_\nu (R > \sigma) \), the soft potential
contribution to the shear viscosity, is identical to the expression derived by Bearman, apart from the limit \( R > \sigma \) appearing in the WD expression.

### 2.5.6. Summary of the Results of the Different Theories

For purposes of comparison, we will consider only the coefficient of shear viscosity of a binary liquid mixture, and rewrite the preceding results in the accompanying tabular form, where \( \varphi_a \) and \( \eta_a \) are meant to represent the partial fluidity and viscosity, including the specific proportionality factors of each theory. In the second column, the results are reduced to the expressions for the corresponding ideal mixtures, from which all deviations are measured. The excess functions are then defined by

\[
\eta^E = \eta_M - \eta^\text{Ideal}_M, \quad \varphi^E = \varphi_M - \varphi^\text{Ideal}_M
\]  

<table>
<thead>
<tr>
<th>Theory</th>
<th>( \varphi_M = \sum_a x_a \varphi_a )</th>
<th>( \eta_M = \sum_a x_a \eta_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Eyring:</td>
<td>( \eta^{-1}_M = \sum_a x_a \eta_a^{-1} )</td>
<td>( \eta^\text{Ideal}_M = \sum_a x_a \eta^\text{Ideal}_a )</td>
</tr>
<tr>
<td>2. RASSD:</td>
<td>( \eta_M = \sum_a x_a \eta_a )</td>
<td>( \eta^\text{Ideal}_M = \sum_a x_a \eta^\text{Ideal}_a )</td>
</tr>
<tr>
<td>3. CR:</td>
<td>( \eta_M^2 = \sum_a x_a \eta_a^2 )</td>
<td>( \eta^\text{Ideal}_M = \sum_a x_a^2 \eta^\text{Ideal}_a )</td>
</tr>
<tr>
<td>4. BJ:</td>
<td>( \eta_M = \sum_a x_a \eta_a )</td>
<td>( \eta^\text{Ideal}_M = 2 \sum_a x_a \eta^\text{Ideal}_a )</td>
</tr>
</tbody>
</table>

There are some essential differences between these results which should be pointed out. First, as already noted, the partial viscosities in the RASSD and the BJ expressions, (65) and (105a), contain an explicit dependence on the diffusion coefficients, while there is no such dependence in the CR theory or in the relation obtained from the Eyring theory. Second, there are explicit mass dependences only in the RASSD and the CR expressions (68) and (102). In the RASSD result, the mass factor is "weighted" by a factor involving the differences in the molecular energies and diameters of the components. It may be shown that the viscosity of the mixture is relatively insensitive to large mass deviations \( \frac{1}{2} < m_a/m_\beta < 2 \) [82]. This implies that the most important factors are, in fact, the molecular parameters \( \epsilon \) and \( \sigma \). Indeed, it may be
shown that, for instance, a small modification of the molecular diameters (|ρ| = 0.1) leads to an inversion of the sign of the RASSD excess viscosity, while the same change in parameters does not qualitatively alter the excess fluidity predicted from the Eyring theory [82].

The WD results cannot be put into a simple form for comparison since the kinetic contribution is quite complicated. However, it has already been remarked that the soft potential contribution \( \eta_ν(R > σ) \), is identical in form with the BJ expression for the viscosity. The advantage of the WD theory over that of BJ is, of course, the advantage of Rice and Allnatt's procedure—which accounts for short-range strongly repulsive collisions as well as soft interactions—over the earlier Kirkwood theory which did not allow for the hard collisions.

2.6. COMMENTS ABOUT MORE COMPLEX LIQUIDS

This review is concerned with the properties of simple liquids. Even among this group there are a few polyatomic molecules (CO, N\(_2\), O\(_2\), CH\(_4\), H\(_2\)) and any satisfactory discussion of these cases must include an analysis of the coupling between the internal degrees of freedom and translational motion, since it is this interaction which leads to deviations from the behavior characteristic of monatomic liquids. These deviations are conveniently classified into two categories: quantum effects and more direct internal motion effects.

Leaving aside the case of liquid He, there are very few studies of transport phenomena in the liquid state specifically designed to elucidate quantum effects. As a result, only a few qualitative remarks may be made, and most of these must be based on corresponding states arguments with the reduced wavelength of the molecules explicitly included. To examine the nature of the corresponding states argument, consider the reduced transport coefficient \( α^* \) defined by

\[
α^* = α^*(T^*, ρ^*, A^{*2})
\]

with

\[
A^{*2} = \hbar^2/σ^2mε
\]

For two quantum liquids (e.g., 2 isotopes) at the same temperature [and for the sake of simplicity, we consider them along their liquid-vapor equilibrium curve, so that \( α^* = α^*(T^*, A^{*2}) \)] one has the ratio

\[
\frac{α_1(T)}{α_2(T)} = \frac{α^*(T^*_1, A^{*2}_1)}{α^*(T^*_2, A^{*2}_2)} \frac{z_1}{z_2}
\]

\( ^{\dagger} \) The dependence of \( α^* \) on the square of \( A^* \), at least for small and moderate wavelengths, follows from the fact that the expansion of the scattering cross section is even in \( \hbar \).
where \( z_1 \) and \( z_2 \) are combinations of the reduction parameters, and

\[
\alpha^*(T_1^*, \Lambda_1^{*2}) = \alpha^* \left[ T_2^*(1 + \delta), \Lambda_2^{*2} \left( 1 + \frac{\Delta \Lambda^{*2}}{\Lambda_2^{*2}} \right) \right]
\]

(114)

with

\[
\Delta \Lambda^{*2} = \Lambda_1^{*2} - \Lambda_2^{*2}
\]

Expansion of \( \alpha^*(T_1^*, \Lambda_1^{*2}) \) about \( (T_2^*, \Lambda_2^{*2}) \) yields

\[
\frac{\alpha^*(T_1^*, \Lambda_1^{*2})}{\alpha^*(T_2^*, \Lambda_2^{*2})} = 1 - \frac{\delta}{T_2^*} \left( \frac{\partial \ln \alpha^*}{\partial 1/T^*} \right)_{T_2^*} + \Delta \Lambda^{*2} \left( \frac{\partial \ln \alpha^*}{\partial \Delta \Lambda^{*2}} \right)_{\Lambda_2^{*2}}
\]

(115)

where \( (\partial \ln \alpha^*/\partial 1/T) \) is presumed known from experimental data. Provided that \( (\partial \ln \alpha^*/\partial \Delta \Lambda^{*2}) \) can be determined, this result permits the evaluation of the deviation of the property \( \alpha \) from the classical limit. Since the analytical form of the function \( \alpha^*(\Lambda^{*2}) \) is unknown, the wavelength factor must be evaluated graphically from experimental data.

It is clear that the development cited cannot be rigorously correct but, as will be shown in a later section, the corresponding states formalism does permit qualitative estimation of the effects of finite wavelength on some of the transport properties.

Some progress toward a kinetic theory of near classical fluids has been made, at least formally. Applying the weak coupling (linear trajectory) perturbation theory of Ross to the Wigner function, Davis et al. [83] have derived a Fokker-Planck equation including first order quantum effects. McLaughlin et al. [84] have solved this equation for the case of self-diffusion of species \( \alpha \) in a \( v \)-component mixture. They find for the self-diffusion coefficient

\[
D_\alpha = kT/\zeta_\alpha
\]

(115a)

where

\[
\zeta_\alpha = -\sum_{\beta} \rho_\beta \left( \frac{\mu_{\alpha\beta}}{72\pi^5kT} \right)^{1/2} \int_0^\infty k^3 G_{\alpha\beta}(k) \tilde{V}_{\alpha\beta}^{(s)}(k) dk - \frac{k^2}{8\mu_{\alpha\beta} kT} \int_0^\infty k^5 G_{\alpha\beta}(k) \tilde{V}_{\alpha\beta}^{(s)} dk
\]

(115b)

The first term on the right-hand side of this equation is the linear trajectory coefficient \( \zeta^L \) found by Helfand. The second term is the first-order quantum correction to the classical theory. The ratio of the quantum contribution to the classical contribution goes as the square of the de Broglie wavelength divided by the length parameter characteristic of the potential energy function. According to preliminary calculations, the quantum correction is quite significant for liquid neon (10–15% of the total friction coefficient) and is a negative correction.
For the case of molecules with internal degrees of freedom, the available theory and data are very incomplete. Indeed, to date, there are no theoretical analyses available which permit accurate calculation of the transport properties of fluids of polyatomic molecules.* On the basis of the theory developed by Longuet-Higgins et al. [85], practical formulas were obtained by Valleau [86] for the special cases of the thermal conductivity and the viscosity of a dense fluid of rough spheres. The correction factor for the viscosity of rough spheres (R) with respect to smooth spheres (S) is given by

\[
\frac{\eta_R}{\eta_S} = \frac{1 + (7/16)K}{1 + (4/16)K} \quad K = \frac{4I}{m_0^2}
\]  

(116)

where \(I\) is the moment of inertia of the sphere. The thermal conductivity of the rough sphere fluid is simply twice as large as that for the smooth sphere fluid.

---

* Numerous valuable studies have been made by Dahler et al. [87]. Although these investigators have made numerical calculations for the rough sphere and the loaded sphere liquids, based on the Enskog theory, no comparison has been made yet between theory and experiment for real liquids.
TRANSPORT PHENOMENA IN SIMPLE LIQUIDS

Of course, the rough sphere theory may be used to obtain an estimate of the rotational contribution to the fluxes of momentum and energy, as will be seen in the section on the interpretation of experimental data, but no significant calculations can be made because the rough sphere model is such a poor characterization of real molecules.

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3. Experimental Procedures and a Comparison between Theory and Observation*

In this section we attempt to answer two questions:

(a) How well do theory and experiment agree? (b) What are the origins of the discrepancies between theory and experiment?

It is clear that meaningful answers to questions (a) and (b) depend upon the availability and accuracy of experimental data, so that it will be necessary for us to compare data from several sources and, occasionally, to estimate the reliability of the data. We begin by commenting briefly on the experimental methods, and then discuss in detail the interpretation of the data relevant to simple liquids, liquid mixtures, and isotope effects in the liquid phase.

3.1. Experimental Methods

An experimental study of any of the properties of the simple liquids considered in this review requires measurements in the temperature region, say, from 15° to 250°K. The cryogenic techniques required are now very well known, and these temperatures are reached and maintained without great difficulty. Since there exists an extensive literature dealing with cryogenic techniques, and because the different methods used to measure transport coefficients are described in many textbooks, we focus attention herein on only a few aspects of the technical problems encountered in the measurements discussed. Because of its novelty, however, we discuss in somewhat more detail the use of laser technology for the determination of transport coefficients.

Consider first the determination of the shear viscosity. The techniques used may be roughly divided into two categories: stationary state methods and nonstationary state methods. The first class includes capillary flow, falling ball (or cylinder), and rotating cylinder methods. The principle underlying all of the techniques in the second class is the measurement of the damping of an oscillating body (sphere, cylinder, disk, or grid) by the viscous drag.

The capillary flow technique is widely known and easily used at room temperature and atmospheric pressure. However, the necessity of

* Reference citations prefixed by 4 are listed in the bibliography of Section 4.1; all other reference citations refer to the list at the end of this section. This bibliographical survey was completed in December 1965, but we have added a supplement (Section 4.2) covering the year 1966. These references are not included in Tables XVI to XX, and when citations are made in the text they are prefixed by 1966.
pumping the fluid back to the viscometer head introduces problems in a cryogenic environment. To achieve this some investigators have used an inert gas as a pressure transmitting fluid [4-140], while others have used a piston to drive the liquid back to the top of the capillary [1]. Moreover, as usually constructed, the capillary flow viscometer utilizes visual observation, thereby requiring a glass instrument which cannot be used for high pressure measurements.

The pressure dependence of the shear viscosity is most easily determined using damped oscillator techniques, since then no transducer seals for moving parts need be introduced into the apparatus. In addition, damped oscillator techniques have the advantage (in principle) of yielding absolute measurements of the product \( \eta \rho \). In contrast, capillary viscometry usually implies measurement relative to some standard known viscosity because of the difficulty of making precise end corrections and flow velocity corrections. To be fair, it should be noted that unless the shape of the oscillating body is carefully chosen the solution to the equations of motion is very complex and end corrections are tricky to obtain accurately [2].

The other coefficient of viscosity, the dilatational viscosity, has been measured in only one fashion. This involves the determination of the attenuation of sound by pulse techniques [4-112], and therefrom finding the ratio of the excess sound absorption to the classical sound absorption due to the finite thermal conductivity and shear viscosity of the liquid. The accuracy achieved at present is relatively poor, but it appears likely to be improved in the near future.

The selection of a method to be used in measuring thermal conductivity reduces to a choice between two steady state techniques, as the calculations involved in the nonsteady state methods are either very tedious or inaccurate. Of the two commonly used geometries, horizontal parallel plates and vertical concentric cylinders, neither seems to possess a marked advantage in inherent accuracy. However, the parallel plate geometry requires high precision guard heaters to insure accurate measurements, while the concentric cylinder geometry can be used without the necessity for such precautions. When one adds to the usual requirements a restriction on the horizontal diameter so that the cell can fit into a high pressure bomb which itself must fit into a Dewar for cooling purposes, the choice is necessarily narrowed to the concentric cylinder geometry [4-77, 4-162].

In addition, in this geometry it is relatively easy to eliminate convection currents. In a variant of the coaxial cylinder apparatus (the "hot wire" type of apparatus) a tightly coiled fine filament simulates the inner cylinder [4-171]. Despite the arguments advanced above, some inves-
tigators have preferred the use of a parallel plate apparatus; these investigations have, generally, not included high pressure measurements [4-121, 4-123].

The determination of the self-diffusion coefficients of the fluids considered herein by the nuclear spin-echo method is hindered by the lack of suitable isotopes, though it has been successfully used for the case of methane [4-55, 4-103, 4-142]. When measurements at low temperatures and over a large pressure range are required, the open end capillary technique of Anderson and Saddington [3] appears most suitable. This is indeed the method employed by the two groups which have measured the self-diffusion coefficients of liquefied Ar, Kr, Xe, and CH₄ [4-28, 4-29, 4-180].

At present there exist only two or three experimental studies of the ionic mobility in simple liquids (excluding He). The ionic mobility of a charged particle is defined as the ratio of the ionic drift velocity to the applied electric field. Davis et al. [4-38, 39] have used small fields (<250 V cm⁻¹) in order to obtain field-independent mobilities. The ions were produced by the alpha radiation emitted from a Po²¹⁰ source. On the other hand, Henson [4-67] has made measurements up to 4300 V cm⁻¹, using field ionization from a tungsten point immersed in the liquid. Wherever comparison is possible, the results obtained from the two methods of ion production are in agreement with one another.

With the development of lasers, a new technique for the measurement of transport coefficients has become available. The radiation from a laser is coherent and spread over a very small frequency range. Because of these characteristics it is possible to determine the broadening of the Rayleigh component of radiation scattered from a fluid, and this line broadening is determined by the classical transport coefficients η, κ, and φ. To understand the phenomena involved it is necessary to discuss some aspects of the theory of light scattering.

Consider a transparent fluid medium on which an electromagnetic wave is incident. Even though the fluid is transparent at the frequency of the incident radiation, there is attenuation of the beam as it traverses the fluid. For there exists in any medium fluctuations in density which, in turn, give rise to fluctuations in the dielectric constant. Consider the liquid to be spanned by a lattice which divides it into cells the linear dimensions of which are small relative to the wavelength of the radiation but large relative to the range of intermolecular forces. Because the configuration space correlations between molecules are of the range of the intermolecular forces, it is valid to assume that density fluctuations in each of the subvolumes are independent, and therefore that if each cell acts as a secondary source of radiation, all such sources are to be
regarded as incoherent with respect to each other. Now, each cell does act as a source of radiation because a density fluctuation implies that in the presence of an external field there will be a point-to-point variation in the polarization of the medium. Interpreting the polarization in terms of a dipole moment per unit volume, and recalling that the intensity of dipole radiation depends upon the square of the dipole moment, it is seen that the intensity of scattered radiation does not vanish even though the average density is the same throughout the fluid. Indeed, it is clear that the intensity of the scattered radiation depends on the mean square fluctuation in density or mean square fluctuation in dielectric constant. Of course, the scattered radiation may also contain a Raman component of different frequency from the incident light, resulting from a change in the quantum state of the molecule on which the light falls. In a liquid, the rotational motion is effectively quenched, so that only vibrational (or electronic) Raman lines may be seen. The rotation of molecules leads to a relatively broad line whose intensity at the frequency of the incident light may be considered to be a contribution to Rayleigh scattering. Clearly, the quenching of the rotational motion and the consequent character of the scattered radiation imply that the possibility of separating out of the total Rayleigh scattering a fraction due to thermodynamic fluctuations depends on the magnitudes of the relaxation times for the associated processes. It is necessary that the relaxation times for all processes required to establish thermodynamic equilibrium be small relative to the times required to create the fluctuations of interest. In this case, the scattered radiation consists of a narrow unshifted line and a broad background.

Assuming that these conditions are met, it must be recognized that the “unshifted line” in fact has a fine structure. The origin of the fine structure is in the nature of the thermodynamic fluctuations. Any given density fluctuation may be considered to be composed of an adiabatic fluctuation in pressure and a fluctuation in entropy, since the density may be regarded to be a function of the internal energy and the entropy of the fluid. Now an adiabatic fluctuation in density corresponds to a pressure pulse which will be transmitted as a sound wave. Fourier analysis of the dielectric constant then shows that the scattered radiation has two components separated by $\Delta \omega_0$ from the incident light

$$\Delta \omega_0 = \pm (2\omega u/c) \sin(\theta/2)$$

(117)

where $u$ is the velocity of sound, $c$ the velocity of light, and $\theta$ the scattering angle. Note that the frequency separation depends on the scattering angle. In contrast with this result, fluctuations of entropy at constant pressure are not propagated relative to the fluid, so that this
fluctuation gives rise to an undisplaced line. The spectrum of Rayleigh scattering is therefore seen to have three components. By the use of simple thermodynamic arguments it is readily shown that the ratio of the intensities of the displaced doublet to the total scattering is just $C_v/C_p$, valid when the temperature dependence of the dielectric constant may be neglected.

Since we have interpreted the origin of the Rayleigh-Brillouin-Mandelstam spectrum in terms of the propagation of fluctuations, it is clear that the line shape depends on the details of the propagation process. Assuming that fluctuations decay exponentially with time constant $\gamma$, i.e., as $\exp(-\gamma t)$, the intensity distribution within a line is

$$dI = \frac{I_0}{\pi} \frac{\gamma}{(\Delta \omega - \Delta \omega_0)^2 + \gamma^2} d\Delta \omega$$  \hspace{1cm} (118)$$

with $I_0$ the total intensity of the line. From the theory of sound absorption

$$\gamma = \frac{q^2}{2\rho} \left[ \frac{4\eta + \phi + \kappa}{C_v} \right]$$  \hspace{1cm} (119)$$

with $q$ the wave vector of the sound wave. For the width of the doublets, where $q^2 = 2(\omega/c)^2(1 - \cos \theta)$, it is found that

$$\gamma = \frac{\omega^2}{\rho c^2} (1 - \cos \theta) \left[ \frac{4\eta + \phi + \kappa}{C_v} \right]$$  \hspace{1cm} (120)$$

Correspondingly, the decay of the central peak is determined by the thermal conductance, and it is found that

$$\gamma = \frac{2\kappa}{\rho C_v} \left( \frac{\omega}{c} \right)^2 (1 - \cos \theta)$$  \hspace{1cm} (121)$$

and the shape is given by the formula for $dI$ (with $\Delta \omega_0 = 0$) displayed above.

As of the date of preparation of this review experiments have only been carried out on fluids near the critical point, where the intensity of scattering is very large. There appears little doubt, however, that the available frequency measurement techniques can be improved and that the study of light scattering can be extended to provide measurements of transport coefficients of accuracy comparable with that obtained using classical methods.

3.2. SIMPLE LIQUIDS

We have already mentioned that in the case of simple liquids the most commonly measured transport property is the shear viscosity. Indeed,
there are data available from a number of laboratories, so that both the reproducibility and accuracy of the data may be assessed. Illustrations of how well different measurements agree are given in Fig. 1 for three different examples: a liquid of monatomic molecules (Ar), a liquid of diatomic molecules (O₂), and a liquid of roughly spherical polyatomic molecules (CH₄). Fewer measurements of the thermal conductivity have been made, so that a comparison between different sources is not always possible and, when made, the reproducibility of the results is not as obvious as for the case of the shear viscosity. It is often found that nonnegligible discrepancies remain between the results of different investigators. Despite the inadequacies of the available data, there are enough measurements of \(\kappa\) and \(\eta\) that detailed analysis of all the data will not be undertaken herein.*

The self-diffusion coefficient is known only for a few simple liquids: Naghizadeh and Rice [4-108] studied argon, krypton, xenon, and methane, while Cini-Castagnoli reported one measurement in liquid argon at 84.5°K (Cini-Castagnoli and Ricci [4-29]) (which is in fairly good agreement with the measurements of Naghizadeh and Rice), and a few measurements of liquid CO [4-28]. The diffusion coefficient of liquid CH₄ has also been deduced from spin-echo measurements [4-55, 4-103, 4-142].

*Note added in proof: Data for \(\eta\) as a function of pressure in Ar and O₂ have been reported by De Bock, Gravendock, and Awouters [7a].
Fig. 2. The reduced viscosity as a function of the reciprocal reduced temperature: (+) Ar, (∗) Kr, (●) Xe, (△) CO, (▽) N₂, (□) O₂, and (○) CH₄.

Fig. 3. The reduced thermal conductivity as a function of the reduced temperature. Key same as that for Fig. 2.
The only experimental determination of the bulk viscosity of which we are aware is in liquid argon, and was recently reported by Naugle and Squire [4-111-4-113].

The mobilities in liquid Ar, Kr, and Xe have been studied experimentally by Davis et al. [4-38, 4-39] and by Henson (Ar), who has also measured the mobility of positive ions in liquid nitrogen [4-67]. Henson's results for liquid Ar are in agreement with those of Davis et al.†

Consider now the interpretation of the experimental results cited, in terms of the theories sketched in Section 2. Correlations between various properties of liquids (and gases) are often sought in terms of the theorem of corresponding states. Given that this principle satisfactorily correlates the equilibrium properties of many liquids, its extension to the description of transport phenomena is a natural first step in the analysis of experimental data. Moreover, as has been shown in Section 2.4, if the intermolecular potential is adequately represented as a sum of pair potentials, a unique and rigorously defined corresponding states analysis is possible.

The transport coefficients for all the liquids considered herein have been reduced using the critical point values of the temperature, pressure, and density. The resulting values of $\eta^*$, $\kappa^*$, and $D^*$ are displayed as a function of the reduced temperature $T^*$ in Figs. 2–4. Examination of

* Note added in proof: Measurements have recently been reported by Naugle, Lunsford, and Singer [4-112], and by Madigorsky [24a].

† A complete bibliography of publications dealing with the transport properties of simple liquids is given in Section 4.1.
these figures clearly shows that the transport coefficients are much more sensitive to details of the intermolecular interaction, its shape, angular dependence, etc., than are the equilibrium properties of the liquid. Indeed, as expected, the correspondence between the properties of Ar, Kr, and Xe is verified, but the properties of these substances cannot be brought into correspondence with those of diatomic molecules. Similarly, the properties of CO and N\textsubscript{2} are in rough correspondence (these molecules are isoelectronic, so this is not unexpected), but differ substantially from the properties of O\textsubscript{2}.\footnote{The self-diffusion coefficient of CO seems to be in correspondence with those of Ar, Kr, and Xe, but detailed examination of the data reveals a deviation of about 10\% \cite{4,28}.} Methane, which is usually considered to be a "nearly spherical" molecule, and for which the equilibrium properties of the liquid are in correspondence with the equilibrium properties of Ar, Kr, and Xe, clearly has an intermolecular pair potential different enough from that of Ar, Kr, and Xe that no correspondence between the transport coefficients can be found. This observation emphasizes even more clearly the sensitivity of transport coefficients to details of the intermolecular potential. It is to be expected that the repulsive part of the pair potential in CH\textsubscript{4} is steeper (relative to the molecular diameter) than the corresponding core potentials in Ar, Kr, or Xe. The steepness arises from the averaging of the potential over the positions of all the peripheral atoms in the molecule. That is, the intermolecular spacing in the liquid is determined by the molecular diameter, but the repulsive forces arise from short-range overlaps at the periphery of the molecule. The observed pressure dependence of the self-diffusion coefficient in CH\textsubscript{4} deviates from that of Ar, Kr, and Xe in the direction required by the presence of a steeper repulsive potential. A further confirmation of the preceding observation is obtained when the molecular parameters determined from liquid viscosity data are compared with those obtained from other sources: Agreement is found for Ar, Kr, and Xe, while for the other substances the discrepancies between different sources of the parameters exceed the experimental errors \cite{4,15}.

Consider, now, the temperature dependence of the transport coefficients. It is well known that the self-diffusion and the viscosity coefficients are exponential functions of $T^{-1}$ at constant pressure and over a limited range of temperature.\footnote{This is a very accurate description between the triple point and the N.B.P. We also notice that $\eta$ decreases, while $D$ increases, with increasing temperature.} The activated state and cell model theories (see Section 2.1) are particularly successful in reproducing the form

$$\eta = A \exp(B/T)$$

(122)
with $A$ and $B$ constants, but they cannot explain the relative insensitivity of the viscosity to temperature under conditions of constant volume. The free volume theory of Cohen and Turnbull [4] accounts for the constant volume temperature dependence satisfactorily (the free volume is, to first approximation, a function of density only) but requires the use of two adjustable parameters. There can be no doubt that the theories of this group are useful and successful parameterized representations of experimental data, but the parameters cannot be quantitatively interpreted in terms of the structure of the liquid.

There is, in the Eyring model (Kincaid et al. [5]), a relationship between the shear viscosity and the heat of vaporization. For, in this model, both vaporization and fluid flow require that a molecule acquire sufficient energy to "break bonds" before it can leave an equilibrium position. Eyring et al. showed, by averaging the data for a large number of systems, that the ratio $\frac{\Delta E_{\text{vap}}}{\Delta G^*}$ is 2.45, where $\Delta G^*$ is defined in Eq. (54) and $\Delta E_{\text{vap}}$ is the energy of vaporization. An application of this argument to the case of simple liquids reveals a further inadequacy in the activated state model: As shown in Table I the ratio $L/B$, where $B$ is defined in Eq. (122) and $L$ is the heat of vaporization, is not at all constant.

<table>
<thead>
<tr>
<th></th>
<th>Argon</th>
<th>Nitrogen</th>
<th>CO</th>
<th>Oxygen</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$ (kcal/mole)</td>
<td>1.404</td>
<td>1.333</td>
<td>1.411</td>
<td>1.629</td>
<td>1.820</td>
</tr>
<tr>
<td>$L/B$</td>
<td>2.9</td>
<td>2.6</td>
<td>3.0</td>
<td>4.2</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The Rice-Allnatt theory (Section 2.2) predicts that at constant density the shear viscosity is little affected by changes in temperature, and Lowry et al. [4-98] have shown that, in view of the sensitivity of the theory to the imperfectly known radial distribution function, this prediction is in agreement with Zhdanova's results for liquid argon [4-177] (see Table II).

In Table III experimental values of the shear viscosity of liquid argon are compared with the predictions of the RA theory, the WD modification [Eq. (106)] of the RA theory, and the PNM theory [Eq. (34b)]. The truncated Lennard-Jones potential, with $\sigma = 3.36 \text{ Å}$ and $\epsilon/k = 123.2^\circ$K, was assumed and the theoretical pair correlation function, computed by Kirkwood et al. [6] on the basis of the superposition approximation, was
TABLE II
Comparison of Theoretical and Observed Temperature Dependence of the Shear Viscosity of Liquid Argon at Constant Density ($\rho_n = 1.12$ gm cm$^{-3}$)$^a$

<table>
<thead>
<tr>
<th>State</th>
<th>$128^\circ$K</th>
<th>$133.5^\circ$K</th>
<th>$185.5^\circ$K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 atm</td>
<td>100 atm</td>
<td>500 atm</td>
</tr>
<tr>
<td>$\eta(\text{obs})_T$</td>
<td>1.00</td>
<td>1.01</td>
<td>1.04</td>
</tr>
<tr>
<td>$\eta(\text{calc})_T$</td>
<td>1.00</td>
<td>1.005</td>
<td>1.06</td>
</tr>
</tbody>
</table>

$^a$ After Lowry et al. [4-98].

used for all the calculations. Except for the value at $90^\circ$K, the RA and WD predictions are within 17% of the experimental viscosities, the WD predictions being slightly better than the RA predictions. The PNM predictions are low by about 40% for all comparisons made in Table III; nevertheless, the predicted temperature dependence agrees rather well with experiment. Thus, as was anticipated, the PNM theory, which neglects kinetic contributions and part of the potential contributions to the transport coefficients, predicts viscosities that are much too small.

The temperature dependence of the thermal conductivity deviates slightly from linearity in the temperature region up to the critical temperature, in the direction such that it decreases with increasing temperature. We also note that the magnitude, and the pressure and the temperature dependences of $\kappa$, all decrease in the following order:

TABLE III
Shear Viscosity of Liquid Argon in Millipoise

<table>
<thead>
<tr>
<th>State</th>
<th>90°K</th>
<th>120°K</th>
<th>128°K</th>
<th>133.5°K</th>
<th>136.3°K</th>
<th>149.4°K</th>
<th>185.5°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.3 atm</td>
<td>12.3 atm</td>
<td>50 atm</td>
<td>100 atm</td>
<td>26.8 atm</td>
<td>45.5 atm</td>
<td>500 atm</td>
</tr>
<tr>
<td>$\eta(\text{obs})^a$</td>
<td>2.39</td>
<td>1.13</td>
<td>0.835</td>
<td>0.843</td>
<td>0.770</td>
<td>0.510</td>
<td>0.869</td>
</tr>
<tr>
<td>$\eta(\text{calc})^b$</td>
<td>1.41</td>
<td>—</td>
<td>0.692</td>
<td>0.701</td>
<td>—</td>
<td>—</td>
<td>0.874</td>
</tr>
<tr>
<td>$\eta(\text{calc})^c$</td>
<td>1.90</td>
<td>—</td>
<td>0.86</td>
<td>0.85</td>
<td>—</td>
<td>—</td>
<td>1.030</td>
</tr>
<tr>
<td>$\eta(\text{calc})^d$</td>
<td>1.33</td>
<td>0.88</td>
<td>—</td>
<td>—</td>
<td>0.62</td>
<td>0.43</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ After Lowry et al. [4-98] and Cook [4-34].

$^b$ The RA theory.

$^c$ The WD modification of the RA theory.

$^d$ The PNM theory.
TRANSPORT PHENOMENA IN SIMPLE LIQUIDS

CH₄, Ar, Kr, and Xe [4-77]. Above 100 atm the coefficient of thermal conductivity seems to increase almost linearly with the pressure and we mention that, according to Ikenberry and Rice [4-77], \((\partial\kappa/\partial p)_T\) for CH₄ is considerably larger than for Ar, Kr, and Xe. These investigators tested the Rice-Allnatt theory against their experimental results and found good agreement (~10%) (see Table IV). Also entered in Table IV

### TABLE IV

<table>
<thead>
<tr>
<th>State</th>
<th>90°C K</th>
<th>120.3°C K</th>
<th>128°C K</th>
<th>133.5°C K</th>
<th>136.3°C K</th>
<th>149.4°C K</th>
<th>185.5°C K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm</td>
<td>1.3 atm</td>
<td>12.3 atm</td>
<td>50 atm</td>
<td>100 atm</td>
<td>26.8 atm</td>
<td>45.5 atm</td>
<td>500 atm</td>
</tr>
<tr>
<td>(\kappa(\text{obs}))(^a)</td>
<td>29.6</td>
<td>19.9</td>
<td>18.9</td>
<td>18.6</td>
<td>15.1</td>
<td>13.1</td>
<td>18.7</td>
</tr>
<tr>
<td>(\kappa(\text{calc}))(^b)</td>
<td>16.5</td>
<td>—</td>
<td>16.9</td>
<td>15.9</td>
<td>—</td>
<td>—</td>
<td>17.0</td>
</tr>
<tr>
<td>(\kappa(\text{calc}))(^c)</td>
<td>14.7</td>
<td>—</td>
<td>12.8</td>
<td>12.2</td>
<td>—</td>
<td>—</td>
<td>11.9</td>
</tr>
<tr>
<td>(\kappa(\text{calc}))(^d)</td>
<td>17.7</td>
<td>12.0</td>
<td>—</td>
<td>—</td>
<td>8.3</td>
<td>5.0</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) Units of \(\kappa\) are \(10^{-5}\) cal/sec cm °K.
\(^b\) Ikenberry and Rice [4-77].
\(^c\) The RA theory.
\(^d\) The WD modification of RA theory.
\(^e\) The PNM theory.

are the thermal conductivity coefficients obtained from the WD modification of the RA theory. Contrary to the situation with viscosity, the WD thermal conductivity theory does not agree with experiment (~35% error) as well as the original RA theory.

Examination of the Rice-Allnatt theory shows that one of the major theoretical problems is the determination of the self-diffusion coefficient, not only because diffusion is a purely kinetic phenomenon but also because the Rice-Allnatt determination of the other transport properties depends strongly on the value of the friction coefficient, i.e., on \(D\). The experimental results of Naghizadeh and Rice [4-108] are seen to fit very well the expected linear relationship for the isobaric temperature dependence of the logarithm of \(D\). They also observe experimentally that the self-diffusion coefficient decreases exponentially with increasing pressure at constant temperature and that, in contrast to the thermal conductivity, \((\partial D/\partial p)_T\) is much smaller for CH₄ than for Ar, Kr, and Xe. Examination of the values of \((\partial D/\partial p)_T\) if expressed in terms of an activation volume [4-108], tends to show, as in the case of the viscosity, that there exists no consistent relationship between molar volume and activation volume. Together with the failure of the analogy
with vaporization phenomena, these data seem to rule out any simple activated state model for the diffusion process.

The major failure of the Cohen-Turnbull free volume theory [4] when applied to the case of diffusion in simple liquids is in accounting for the temperature dependence of $D$. Further tests, attempted by Naghizadeh and Rice, lead to the conclusion that this failure is most probably linked to the nature of the intermolecular potential, and measures the deviation of the potential function of the real substance considered from that of the model hard sphere fluid. On the other hand, the dense square-well fluid (Davis et al. [7]) provides a useful zeroth order approximation to the behavior of real fluids. Despite the lack of quantitative agreement for the case of a simple exponential decay of the velocity autocorrelation function, the predicted temperature dependence of $D$ is excellent. If it is assumed that the velocity autocorrelation function does not have an exponential decay, but rather numerical integration is used to obtain $D$, results identical with those obtained from the exponential decay ansatz are obtained. Prior belief that numerical integration led to a better answer than the exponential decay form resulted from a fortuitous cancellation in a series expansion. The question was resolved by McLaughlin and Davis (Section 2 [88]) who showed that $D$ obtained from the Chapman–Enskog type solution of the kinetic

### TABLE V

**Self-Diffusion Coefficient for Liquid Argon**

<table>
<thead>
<tr>
<th></th>
<th>84°K</th>
<th>90°K</th>
<th>100°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$(obs)$^a$</td>
<td>1.84</td>
<td>2.35</td>
<td>3.45</td>
</tr>
<tr>
<td>$D$(calc)$^b$</td>
<td>1.43</td>
<td>1.80</td>
<td>2.25</td>
</tr>
<tr>
<td>$D$(calc)$^c$</td>
<td>1.43</td>
<td>1.80</td>
<td>2.25</td>
</tr>
<tr>
<td>$D$(calc)$^d$</td>
<td>3.91</td>
<td>4.11</td>
<td>—</td>
</tr>
<tr>
<td>$D$(calc)$^e$</td>
<td>2.25</td>
<td>2.49</td>
<td>—</td>
</tr>
<tr>
<td>$D$(calc)$^f$</td>
<td>2.80</td>
<td>3.25</td>
<td>3.85</td>
</tr>
<tr>
<td>$D$(calc)$^g$</td>
<td>2.50</td>
<td>2.75</td>
<td>3.40</td>
</tr>
</tbody>
</table>

* Units of $D$ are $10^{-5}$ cm$^2$ sec$^{-1}$.
^b Naghizadeh and Rice [4-108].
^c Square well, exponentially decaying correlation function.
^d Square well, numerical integration.
*e Small step diffusion theory.
^f Small step, isotope separation data.
^g Linear trajectory, neglecting cross correlations.
^h Linear trajectory theory, including "two-body" cross correlations.
equation is identical with that deduced by Longuet-Higgins and Valleau (see Table V).

Davis and Luks [4-37a] and Luks et al. [4-99] have recently used the square-well model with great success for extensive computations of all the transport properties of liquid Ar, Kr, and Xe. Although the square-well potential is certainly unrealistic, it does have the major features of a realistic pair potential. One interesting result of these calculations is the following. Let the transport property \( \alpha (= \eta, \kappa) \) be the sum \( \alpha = \alpha_v + \alpha_K + \alpha_{Kn} \). Then the kinetic contribution \((\alpha_K)\) and the coupling term \((\alpha_{Kn})\) are shown to represent from about 10 to 30\% of \( \alpha \) for simple liquids.* Another theory which has recently been reexamined is the Rice-Kirkwood small step diffusion theory: The poor agreement between experiment and the small step diffusion theory [7] can be considerably improved when the average Laplacian of the intermolecular potential is evaluated from isotope separation data, as suggested by Friedman and Steele [4-51] and by Boato et al. [4-10] (see Table V).

Using the theoretical pair correlation function computed by Kirkwood et al. [6] on the basis of the superposition approximation, Davis and Palyvos (Section 2 [25, 26]) have compared Helfand’s (Section 2 [24]) linear trajectory theory of self-diffusion, for which \( D = kT/(\xi_s + \xi_H) \), with their extension [see Eq. (29a)], for which \( D = kT/(\xi_s + \xi_H + \xi_{S,H}) \). As seen in Table V, the Davis and Palyvos (DP) theory gives a slight improvement over the original linear trajectory theory. However, in their article Davis and Palyvos concluded, after comparing the theories over the entire temperature range of liquid argon, krypton, and xenon, that the over-all agreement between theory and experiment is not significantly improved by including the cross coefficient \( \xi_{S,H} \). They also concluded that the agreement between theory and experiment for the linear trajectory theory is as good as that of either the Rice-Kirkwood small step diffusion theory or the Douglass theory [9], which results in a formula differing from the RK formula by a factor of \( \pi/2 \). Of course, the theoretical predictions of Davis and Palyvos are based on approximate values for the pair correlation function. Thus, their conclusions are subject to change if more reliable pair correlation functions become available.

We now turn briefly to the study of ion mobility in simple liquids. To date, the literature on this subject is almost entirely limited to the experimental and theoretical study by Davis et al. [4-38, 39] on the mobilities of positive and negative ions in liquid Ar, Kr, and Xe. We therefore refer the interested reader to the details presented in the

* Note that the importance of the contributions to \( \eta \) and \( \kappa \) of terms other than those arising from intermolecular potential energy was previously predicted from the Rice-Allnatt theory.
For our purposes it is sufficient to mention that the experimental data indicate that the mobility varies linearly, but very smoothly, with the external pressure, while the logarithmic dependence of the product $\mu T$ can be represented adequately by the Einstein relation:
\[
\frac{\mu_i}{D_i} = \frac{q}{kT}
\]
with
\[
D_i = A' \exp(-B'/T)
\]

where $q$ is the electronic charge and $D_i$ the diffusion coefficient of the ion. The magnitude, the pressure dependence, and the temperature dependence of the positive ion mobility in liquid Ar, Kr, and Xe can be quantitatively accounted for by the Rice-Allnatt theory, and the agreement with experiment is very satisfactory if the positive ions are $\text{Ar}_2^+$, $\text{Kr}_2^+$ or $\text{Xe}_2^+$, while it is much poorer if a different ionic species (say, $\text{Ar}^+$, f.i.) is postulated. On the other hand, the study of negative ions is much more difficult because of impurity effects.* Indeed, Davis et al. interpret their mobility data in terms of the properties of the $\text{O}_2^-$ ion, and, if it may be assumed that the negative charge carriers in liquid Ar, Kr, and Xe are effectively $\text{O}_2^-$ ions, the Rice-Allnatt theory is again seen to provide an adequate representation of the observations.

Finally, consider the coefficient of bulk viscosity; $\phi$ can be determined from the excess ultrasonic attenuation (excess over that due to shear viscosity and thermal conductivity) and the only available data are for liquid argon at $84^\circ$, $87^\circ$, $90^\circ$, and $112^\circ$K at pressures up to 10 atm [4-111, 4-113].

These measurements were made very recently by Naugle and Squire, who observe that the ratio $\phi/\eta$ increases from 0.66 to 1.4 between $84^\circ$ and $112^\circ$K. This last value was correctly predicted by Rice and Gray [4-61] from the Rice-Allnatt theory; for instance, $(\phi/\eta)_{\text{calc}} = 1.3$ at $128^\circ$K, which is a remarkable result in view of the unavoidable uncertainties in the radial distribution function, its density dependence, and the pair potential. In contrast, the calculated value at $90^\circ$K is far too large:
\[
(\phi/\eta)_{\text{calc}}:90^\circ\text{K} = 4; \quad (\phi/\eta)_{\text{obs}}:90^\circ\text{K} = 0.69
\]

As in other cases, the failure of the theory at $90^\circ$K is attributable to the poor quality of the available pair correlation function. In view of the uncertainties in both the theoretical ($\pm 20\%$) and the experimental ($\pm 50\%$) values of $\phi/\eta$, no definitive conclusions can be drawn without

* Because such high purity is required (carrier densities are only of order $10^5 \text{cm}^{-3}$) it is extremely difficult to eliminate all impurities, and measurements of electron mobility in liquid Ar have only recently been obtained [10].
Further experimental information. Finally, we note that no frequency dependence of the attenuation was observed in the range used (30 to 70 Mc/sec).

Note added in proof: More recent measurements [4-112] show that $\phi/\eta$ is constant to ±10% at constant density while the temperature and pressure were varied [4-112]. It is found that $\phi/\eta = 1.2$ at a density of 1.12 gm cm$^{-3}$ (old value 1.4) is still in excellent agreement with theory. $\phi/\eta$ appears to decrease with increasing density, and this is accounted for by theory (Luks, Miller and Davis [4-99]) as shown in Fig. B.

Note added in proof: Recent measurements by Madigosky [24a] of the bulk viscosity of Ar as a function of density from 0.5 to 1.0 gm cm$^{-3}$ at $-38^\circ$C are in quantitative agreement with the predictions of Gray and Rice [4-61]. In more detail, Madigosky reports the following agreement between theory and experiment. (See Fig. C.)

To conclude this examination of all of the transport properties of one-component simple liquids, we wish to discuss briefly the following question, relative to the validity of the Rice-Allnatt theory:

Is the agreement (or disagreement) between theory and experiment significant? This question is very difficult to answer. At present, the available radial distribution functions and potential functions for a dense
FIG. B. Density dependence of $\phi/\eta$. Averages of values at constant density under variable temperature and pressure (●, 50-Mc/sec data; ▲, corrected 30-Mc/sec data). Single data-point calculations or averages of several points at the same temperature and pressure (○, 50-Mc/sec data; △, corrected 30-Mc/sec data; □, results of Naugle (exp.); ■, results of Luks, Miller, and Davis; ○, results of Gray and Rice).

Fluid are extremely poor. For instance, we note that at liquid densities it is not uncommon to have the predicted pressure be negative. Moreover, the pressure is so sensitive to the relative positions of the minimum of $u(R)$ and the first maximum of $g_0^{(2)}(R)$ that a $2\%$ relative shift can change the predicted pressure from $-1000$ atm to $+1$ atm. We have also mentioned, in Section 1, that the equilibrium theory is worst at high densities and low temperatures. For similar reasons it is to be expected that the predicted values of the transport properties at low temperatures and high densities will be furthest from experimental values.

| $\rho_m$ (gm cm$^{-3}$) | $\phi$ (Theory) ($\times 10^4$ poise) | $\phi$ (Expt) ($\times 10^4$ poise) |
|------------------------|--------------------------------------|
| 0.508                  | 1.25                                 | 0.9                                   |
| 0.694                  | 2.33                                 | 2.9                                   |
| 0.812                  | 3.36                                 | 3.3                                   |
| 0.896                  | 4.18                                 | 4.4                                   |
| 0.958                  | 4.91                                 | 4.8                                   |
| 1.008                  | 5.56                                 | 5.6                                   |

* Tables and figures added in proof have been identified alphabetically.
values. It is our opinion that the major contribution to the observed disagreement arises from the inadequacy of the available radial distribution function. It is clear that complete and definitive testing of the Rice-Allnatt theory awaits the determination of very accurate equilibrium distribution functions and potential functions. The presently available agreement between theory and observation suggests (but does not prove) that the Rice-Allnatt theory is a good first-order theory of transport in liquids.

In Table VI we compare the PNM theoretical bulk viscosities with Naugle and Squire's experimental values for argon. The experimental values have been inferred by multiplying experimental shear viscosities by the ratio $\phi/\eta$ measured by Naugle and Squire. The pair correlation function and potential parameters used for the theoretical calculations were those used in computing the shear viscosities in Table III. The

<table>
<thead>
<tr>
<th>TABLE VI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BULK VISCOSITY OF LIQUID ARGON IN MILLIPOISE</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>State</th>
<th>90°K 1.3 atm</th>
<th>110°K 6.58 atm</th>
<th>130°K 20 atm</th>
<th>150°K 47 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$ (obs)$^a$</td>
<td>2.01</td>
<td>1.54</td>
<td>1.96</td>
<td>--</td>
</tr>
<tr>
<td>$\phi$ (calc)$^b$</td>
<td>1.78</td>
<td>1.18</td>
<td>0.66</td>
<td>0.41</td>
</tr>
</tbody>
</table>

$^a$ Inferred from Naugle and Squire's data [4-111-113] for $\phi/\eta$ and experimental shear viscosities [4-34].

$^b$ The PNM theory.

agreement between theory and experiment is not as good as it was for the shear viscosity. The temperature trend is poorly predicted in Table VI.

3.3. LIQUID MIXTURES

The transport coefficients of liquid mixtures have been much less extensively studied than those of the corresponding pure fluids. This unfortunate circumstance will allow us to give a relatively complete review of what has been done in this field, and also to display the available numerical data in Tables VII to XIII, where Exp stands for experimental and ECS stands for Eyring's corresponding states. For the same reason (except for the case of the viscosity of argon-oxygen mixtures) no comparison between different sources can be made. These tables include some original numerical results which have not been published previously.
As early as 1938, Hamman measured the thermal conductivity of nitrogen-oxygen mixtures [4-64]; the validity of these results remains doubtful, since comparison of Hamman's values for pure N₂ and pure O₂ with many more recent measurements show a discrepancy of about 30%. Data on the viscosity of N₂/O₂, N₂/CO, and N₂/CH₄ systems

**TABLE VII**

**Viscosity of Argon-Krypton Mixtures**

\(T = 100.00^\circ\text{K};\ 1 + \delta = 1.39;\ 1 + \rho = 1.07;\ \frac{m_{Kr}}{m_{Ar}} = 2.10\)

<table>
<thead>
<tr>
<th>(x_{Ar})</th>
<th>Exp(^b)</th>
<th>RASSD</th>
<th>ECS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>690</td>
<td>690</td>
<td>690</td>
</tr>
<tr>
<td>0.4</td>
<td>392</td>
<td>398</td>
<td>350</td>
</tr>
<tr>
<td>0.411</td>
<td>302</td>
<td>302</td>
<td>270</td>
</tr>
<tr>
<td>0.6</td>
<td>227</td>
<td>232</td>
<td>217</td>
</tr>
<tr>
<td>0.8</td>
<td>181</td>
<td>181</td>
<td>181</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td></td>
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</tbody>
</table>

\(^a\) The units used are the following: \(\eta\) in \(10^{-5}\) poise; \(\kappa\) in \(10^{-5}\) cal/cm sec \(^\circ\text{K}.\
\(^b\) The first substance mentioned in the table heading is always taken as the reference component for the ratios of the molecular parameters.
\(^c\) The molecular parameters are those obtained from critical data, except for CH₄ and CD₄ (see Section 3.4).
\(^d\) \(X_a\) represents the mole fraction of component \(a\).

\cite{338-stuart-a-rice-jean-pierre-boon-and-h-ted-davis}
**TABLE VIII**

VISCOSITY OF ARGON-METHANE MIXTURES

\((T = 90.91^\circ K; \ 1 + \delta = 1.27; \ 1 + \rho = 1.10; \ m_{CH_4}/m_{Ar} = 0.40)\)

<table>
<thead>
<tr>
<th>(x_{Ar})</th>
<th>Exp(^b)</th>
<th>RASSD</th>
<th>ECS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>198</td>
<td>198</td>
<td>198</td>
</tr>
<tr>
<td>0.2</td>
<td>190</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.204</td>
<td>206</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>188</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.411</td>
<td>210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>192</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.613</td>
<td>219</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>204</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.788</td>
<td>224</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>230</td>
<td>230</td>
<td>230</td>
</tr>
</tbody>
</table>

\(^a\) See footnote \(a\) of Table VII for information.

\(^b\) Boon and Thomaes [4-14].

**TABLE IX**

VISCOSITY OF KRYPTON-METHANE MIXTURES

\((T = 116.00^\circ K; \ 1 + \delta = 0.91; \ 1 + \rho = 1.03; \ m_{CH_4}/m_{Kr} = 0.19)\)

<table>
<thead>
<tr>
<th>(x_{Kr})</th>
<th>Exp(^b)</th>
<th>RASSD</th>
<th>ECS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>106</td>
<td>106</td>
<td>106</td>
</tr>
<tr>
<td>0.25</td>
<td>150</td>
<td>142</td>
<td>134</td>
</tr>
<tr>
<td>0.50</td>
<td>218</td>
<td>203</td>
<td>178</td>
</tr>
<tr>
<td>0.75</td>
<td>317</td>
<td>301</td>
<td>257</td>
</tr>
<tr>
<td>1.0</td>
<td>438</td>
<td>438</td>
<td>438</td>
</tr>
</tbody>
</table>

\(^a\) See footnote \(a\) of Table VII for information.

\(^b\) Boon and Thomaes [4-14].

**TABLE X**

VISCOSITY OF METHANE-DEUTEROMETHANE MIXTURES

\((T = 100.00^\circ K; \ 1 + \delta = 0.991; \ 1 + \rho = 0.996; \ m_{CD_4}/m_{CH_4} = 1.25)\)

<table>
<thead>
<tr>
<th>(x_{CH_4})</th>
<th>Exp(^b)</th>
<th>RASSD</th>
<th>ECS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>173</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>0.5</td>
<td>162</td>
<td>160</td>
<td>159</td>
</tr>
<tr>
<td>1.0</td>
<td>148</td>
<td>148</td>
<td>148</td>
</tr>
</tbody>
</table>

\(^a\) See footnote \(a\) of Table VII for information.

\(^b\) Fontaine-Limbourg et al. [4-47].
### TABLE XI

**Viscosity of Argon-Oxygen Mixtures**

\((T = 84.00°K; \ 1 + \delta = 1.03; \ 1 + \rho = 1.00; \ m_{O_2}/m_{Ar} = 0.80)\)

<table>
<thead>
<tr>
<th>(x_{Ar})</th>
<th>Exp(^{b,c})</th>
<th>RASSD(^d)</th>
<th>RASSD(^e)</th>
<th>ECS(^d)</th>
<th>ECS(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>223(^b,c)</td>
<td>223</td>
<td>223</td>
<td>223</td>
<td>223</td>
</tr>
<tr>
<td>0.200</td>
<td>239(^c)</td>
<td>233</td>
<td>239</td>
<td>234</td>
<td>238</td>
</tr>
<tr>
<td>0.26</td>
<td>234(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.400</td>
<td>248(^c)</td>
<td>244</td>
<td>252</td>
<td>245</td>
<td>252</td>
</tr>
<tr>
<td>0.45</td>
<td>244(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.600</td>
<td>263(^c)</td>
<td>256</td>
<td>265</td>
<td>258</td>
<td>265</td>
</tr>
<tr>
<td>0.61</td>
<td>252(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.74</td>
<td>259(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>271</td>
<td>277</td>
<td>272</td>
<td>277</td>
</tr>
<tr>
<td>0.812</td>
<td>277(^c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.89</td>
<td>283(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>288(^b,c)</td>
<td>288</td>
<td>288</td>
<td>288</td>
<td>288</td>
</tr>
</tbody>
</table>

- \(^{a}\) See footnote \(a\) of Table VII for information.
- \(^{b}\) Fontaine-Limbourg et al. [4-47].
- \(^{c}\) Saji and Okuda [4-144, 4-145].
- \(^{d}\) Calculation made using the molecular parameters as given above.
- \(^{e}\) \((1 + \delta)\) was adjusted to the following values: for RASSD, \((1 + \delta) = 1.04\); for ECS, \((1 + \delta) = 1.06\).

### TABLE XII

**Viscosity of Nitrogen-Carbon Monoxide Mixtures**

\((T = 90.1°K; \ 1 + \delta = 1.05; \ 1 + \rho = 1.01; \ m_{CO}/m_{N_2} = 1.00)\)

<table>
<thead>
<tr>
<th>(x_{N_2})</th>
<th>Exp(^b)</th>
<th>RASSD</th>
<th>ECS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>146</td>
<td>146</td>
<td>146</td>
</tr>
<tr>
<td>0.252</td>
<td>132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.451</td>
<td>127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>0.687</td>
<td>123</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>116</td>
<td>116</td>
<td>116</td>
</tr>
</tbody>
</table>

- \(^{a}\) See footnote \(a\) of Table VII for information.
- \(^{b}\) Gerf and Galkov [4-59].

were reported by Gerf and Galkov in 1940 and 1941 [4-53, 4-58, 4-59], and more recently the group at the Université Libre de Bruxelles [4-11, 4-12, 4-14, 4-47] has measured the viscosity of the Ar/Kr, Ar/CH\(_4\), Kr/CH\(_4\), Ar/O\(_2\), and CH\(_4\)/CD\(_4\) systems. These experiments
TABLE XIII

Viscosity and Thermal Conductivity of Nitrogen-Oxygen Mixtures

\( T = 68.25^\circ K; \quad 1 + \delta = 1.23; \quad 1 + \rho = 0.94; \quad m_{O_2}/m_{N_2} = 1.14 \)

<table>
<thead>
<tr>
<th>( x_{N_2} )</th>
<th>( \eta, \exp^a )</th>
<th>( \eta, \text{RASSD} )</th>
<th>( \eta, \text{ECS} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>384</td>
<td>384</td>
<td>384</td>
</tr>
<tr>
<td>0.4</td>
<td>(354)</td>
<td>316</td>
<td>311</td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>257</td>
<td>256</td>
</tr>
<tr>
<td>0.804</td>
<td>252</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>232</td>
<td>232</td>
<td>232</td>
</tr>
</tbody>
</table>

\( T = 73.2^\circ K \)

<table>
<thead>
<tr>
<th>( x_{N_2} )</th>
<th>( \kappa, \exp^b )</th>
<th>( \kappa, \text{RASSD} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>49.0</td>
<td>49.0</td>
</tr>
<tr>
<td>0.30</td>
<td>47.5</td>
<td>43.0</td>
</tr>
<tr>
<td>0.55</td>
<td>45.5</td>
<td></td>
</tr>
<tr>
<td>0.68</td>
<td>47.5</td>
<td>47.0</td>
</tr>
<tr>
<td>0.85</td>
<td>47.0</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>49.0</td>
<td>49.0</td>
</tr>
</tbody>
</table>

---

\( ^a \) See footnote \( a \) of Table VII for information.

\( ^b \) Galkov and Gerf [4-53]; the value in parentheses does not seem to be reliable.

\( ^c \) Hamman [4-64]; these data are probably erroneous, but were used herein because these are the only available data for the thermal conductivity of a simple liquid mixture.

were undertaken in order to test the theorem of corresponding states and Eyring's model for liquid mixtures, as described in Section 2.5.1. Finally, argon-oxygen mixtures have also been studied by Saji and Okuda [4-144, 4-145] and the deviations—though small—between their data and those of the Brussels' group are not presently understood, since the agreement between the two groups is perfect when the values obtained by both for the viscosities of pure oxygen and pure argon are compared. It is pertinent to mention the existence of data concerning oxygen-ozone mixtures [4-78]: The viscosity of this system seems to be an example of ideal behavior, but the lack of information concerning the molecular properties of ozone renders it impossible to give any further interpretation of the properties of this system at present. Very recently, mutual diffusion experiments have been performed by Ricci [1966-31] on argon, neon, methane, hydrogen and tritium, in liquid nitrogen. Despite the inherent value of such experiments (the first observations of mutual diffusion in simple liquids), a discussion of Ricci's measurements would be quite difficult at the present stage as the data given by the author appear to be "preliminary" results. The need for
increased accuracy can be seen from Table XIV where the coefficients $A$ and $B$ represent the parameters of the exponential variation of $D_{21}$ as a function of the temperature, as observed by the author.

**TABLE XIV**

**Mutual Diffusion in Liquid Nitrogen**

<table>
<thead>
<tr>
<th></th>
<th>$A \times 10^5$ (cm$^2$ sec$^{-1}$)</th>
<th>$B$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>94 ± 8</td>
<td>298 ± 6</td>
</tr>
<tr>
<td>Ar</td>
<td>112.5 ± 3.0</td>
<td>310 ± 5</td>
</tr>
<tr>
<td>Ne</td>
<td>204 ± 8</td>
<td>301 ± 4</td>
</tr>
<tr>
<td>T$_2$</td>
<td>172.5 ± 12.0</td>
<td>296 ± 6</td>
</tr>
<tr>
<td>H$_2$</td>
<td>232 ± 47</td>
<td>309 ± 16</td>
</tr>
</tbody>
</table>

It is important to remind the reader that when we try to explain the behavior of liquid mixtures, whatever the theory employed, we are always forced to assume that the components obey the law of corresponding states (see Section 2.5). Therefore, it is obvious from the analysis in Section 3.2 that the only mixtures which can be (more or less rigorously) tested in this manner are binary systems containing Ar, Kr, and Xe, and the mixture of the diatomic molecules N$_2$ and CO, with the restriction in this last case that the internal degrees of freedom must be taken into account. This latter proviso imposes, at present, an insurmountable theoretical barrier.

Furthermore, we note that it has been shown (see, for example, Boon 4-11) that the molecular parameters obtained from critical data are the most suitable for the study of liquids; these parameters have therefore been used for the calculations reported in this section.

The results of the comparison between experiment and theory are given in tables VII to XIII, and the excess functions (111) are reproduced in Figs. 7 to 14.

Throughout, use has been made of the Rice-Allnatt small step diffusion theory (RASSD, Section 2.5.2) [12a] and of the application of the principle of corresponding states to Eyring’s theory (ECS, Section 2.5.1). Similar comparisons between theory and experiment should be made for the CR (Section 2.5.3) and the BJ (Section 2.5.4) theories (time did not permit the calculations to be carried out). However, because of the similarities between the RASSD, CR, and BJ expressions (110), we are led to expect not very different results from those of the RASSD theory, as already pointed out by Sedgwick and Collins [12] in their treatment of some more complex liquid mixtures.
Note added in proof: Palyvos, Luks, McLaughlin, and Davis [11] have recently compared the square-well theory with the same data. The results, as shown in Figures D, E, and F, and Tables B, and C, are about as good as the RASSD theory.
A first examination of the tables shows that experiment and theoretical predictions are in fairly reasonable agreement. In other words, the calculated absolute values of the transport coefficients of liquid mixtures are of the correct magnitude (within a few percent: 0 to 10%), which is certainly an encouraging result considering the approximations made in the theoretical developments. However, the over-all picture is not as satisfactory when one examines the excess functions, i.e., the deviations from ideal behavior as shown in Figs. 5 to 12. In fact, this is the correct manner in which to check the theory if one wishes to see how differences in the physical nature of the molecules influence the transport properties of the mixtures. Though the senses of the deviations ($\eta^E, \varphi^E > 0$ or $< 0$) are generally reproduced by the theory, large quantitative discrepancies (up to 20%) appear, and therefore each system should be analyzed independently as a function of the molecular characteristics of its components (given in the tables). Since the complete discussion of each separate case would be far too extensive to be reproduced herein, we leave it to the interested reader and instead restrict ourselves to the examination of three characteristic examples.

Consider first the case of argon-krypton mixtures (Fig. 5), the system one expects to provide the most suitable test of the available theories. In this case, there is a remarkably good agreement between the experi-
TABLE B
COMPARISONS OF THEORETICAL SQUARE-WELL SHEAR VISCOSITIES WITH EXPERIMENTS FOR ARGON-METHANE, KRYPTON-ARGON, AND KRYPTON-METHANE LIQUID MIXTURES

<table>
<thead>
<tr>
<th>$x_Ar$</th>
<th>$\eta_{theor} \times 10^3$ (poise)</th>
<th>$\eta_{exp} \times 10^3$ (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Argon-Methane ($T = 90.91^\circ$K)</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>1.96</td>
<td>1.98</td>
</tr>
<tr>
<td>0.204</td>
<td>1.99</td>
<td>2.06</td>
</tr>
<tr>
<td>0.411</td>
<td>2.04</td>
<td>2.10</td>
</tr>
<tr>
<td>0.613</td>
<td>2.11</td>
<td>2.19</td>
</tr>
<tr>
<td>0.788</td>
<td>2.19</td>
<td>2.24</td>
</tr>
<tr>
<td>1.0</td>
<td>2.31</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>Krypton-Argon ($T = 100.0^\circ$K)</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>1.90</td>
<td>1.81</td>
</tr>
<tr>
<td>0.2</td>
<td>2.40</td>
<td>2.27</td>
</tr>
<tr>
<td>0.4</td>
<td>3.00</td>
<td>3.02</td>
</tr>
<tr>
<td>0.589</td>
<td>3.64</td>
<td>3.92</td>
</tr>
<tr>
<td>1.0</td>
<td>5.34</td>
<td>6.90</td>
</tr>
<tr>
<td></td>
<td>Krypton-Methane ($T = 116.0^\circ$K)</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>1.20</td>
<td>1.06</td>
</tr>
<tr>
<td>0.25</td>
<td>1.65</td>
<td>1.50</td>
</tr>
<tr>
<td>0.50</td>
<td>2.30</td>
<td>2.18</td>
</tr>
<tr>
<td>0.75</td>
<td>2.92</td>
<td>3.17</td>
</tr>
<tr>
<td>1.0</td>
<td>4.15</td>
<td>4.38</td>
</tr>
</tbody>
</table>

mental data and the RASSD calculated values, while the ECS theory is in much poorer agreement with experiment.

The nitrogen-carbon monoxide system has also been cited as suitable to test the theory. For $N_2/CO$ the calculations predict, in both cases (ECS and RASSD), almost ideal behavior (Fig. 10), as expected from the relative values of the molecular parameters (the components are isoelectronic, isoenergetic, isodimensional, and isomassive). Though the deviations observed from ideality may be partially due to experimental errors, the discrepancies between theory and experiment are not surprising since the detailed form of the interactions between diatomic molecules is not taken into account in either of the theories.

Another interesting example is provided by the argon-oxygen system (Fig. 9). In this case the "noncorrespondence" of the components seems
TABLE C

Transport Properties and Associated Excess Quantities Predicted by the Square-Well Theory for Liquid Mixtures

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>$x_{Ar}$</th>
<th>$\kappa_T$</th>
<th>$\Delta \kappa$</th>
<th>$\eta$</th>
<th>$\Delta \eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\times 10^4$</td>
<td>$\times 10^4$</td>
<td>$\times 10^3$</td>
<td>$\times 10^3$</td>
</tr>
<tr>
<td>90</td>
<td>0.0</td>
<td>0</td>
<td>4.03</td>
<td>6.41</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-0.590</td>
<td>3.80</td>
<td>-0.0970</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>-0.851</td>
<td>3.61</td>
<td>-0.142</td>
<td>4.44</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>-0.818</td>
<td>3.48</td>
<td>-0.139</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>-0.524</td>
<td>3.39</td>
<td>-0.0901</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0</td>
<td>3.37</td>
<td>0</td>
<td>2.33</td>
</tr>
<tr>
<td>95</td>
<td>0.0</td>
<td>0</td>
<td>3.70</td>
<td>5.83</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-0.554</td>
<td>3.48</td>
<td>-0.0952</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>-0.801</td>
<td>3.31</td>
<td>-0.140</td>
<td>4.04</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>-0.771</td>
<td>3.19</td>
<td>-0.137</td>
<td>3.29</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>-0.495</td>
<td>3.11</td>
<td>-0.0893</td>
<td>2.65</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0</td>
<td>3.10</td>
<td>2.12</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0.0</td>
<td>0</td>
<td>3.42</td>
<td>5.34</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-0.521</td>
<td>3.21</td>
<td>-0.0936</td>
<td>4.47</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>-0.753</td>
<td>3.04</td>
<td>-0.138</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>-0.726</td>
<td>2.93</td>
<td>-0.136</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>-0.467</td>
<td>2.85</td>
<td>-0.0885</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0</td>
<td>2.82</td>
<td>1.90</td>
<td>0</td>
</tr>
</tbody>
</table>

Argon-Krypton

Argon-Methane

<p>| 85      | 0.0     | 0          | 7.43            | 2.25  | 0            |
|         | 0.2     | +0.634     | 6.37            | -0.312 | 2.28       | -0.0431     |
|         | 0.4     | +0.919     | 5.46            | -0.467 | 2.32       | -0.0648     |
|         | 0.6     | +0.890     | 4.72            | -0.466 | 2.39       | -0.0649     |
|         | 0.8     | +0.576     | 4.12            | -0.310 | 2.48       | -0.0433     |
|         | 1.0     | 0          | 3.68            | 2.59  | 0          |
| 90      | 0.0     | 0          | 6.68            | 2.01  | 0          |
|         | 0.2     | +0.597     | 5.74            | -0.286 | 2.04       | -0.0394     |
|         | 0.4     | +0.863     | 4.94            | -0.429 | 2.09       | -0.0593     |
|         | 0.6     | +0.834     | 4.28            | -0.429 | 2.15       | -0.0594     |
|         | 0.8     | +0.539     | 3.77            | -0.286 | 2.24       | -0.0396     |
|         | 1.0     | 0          | 3.37            | 2.33  | 0          |
| 95      | 0.0     | 0          | 6.12            | 1.82  | 0          |
|         | 0.2     | +0.565     | 5.25            | -0.270 | 1.85       | -0.0356     |
|         | 0.4     | +0.816     | 4.52            | -0.405 | 1.89       | -0.0535     |
|         | 0.6     | +0.786     | 3.92            | -0.405 | 1.96       | -0.0535     |
|         | 0.8     | +0.506     | 3.45            | -0.270 | 2.04       | -0.0357     |
|         | 1.0     | 0          | 3.10            | 2.12  | 0          |</p>
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<thead>
<tr>
<th>$T$ (°K)</th>
<th>$x_{At}$</th>
<th>$\kappa \times 10^4$ (cal/cm sec°K)</th>
<th>$\Delta \kappa \times 10^4$ (cal/cm sec°K)</th>
<th>$\eta \times 10^3$ (poise)</th>
<th>$\Delta \eta \times 10^3$ (poise)</th>
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<td>0</td>
<td>0.77</td>
<td>0</td>
<td>0.988</td>
</tr>
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</table>
to be of less importance than the similarity between their molecular parameters (see Table XI). The ECS theory predicts a zero excess function, while an almost zero excess function is predicted by the RASSD theory \((\eta^F/\eta \simeq -2\%)\). The experimental results do not show large deviations from ideality, and an adjustment of the parameters was attempted in order to make the theoretical values fit the experimental data \([4-47]\). An adjustment of just \((1 + \delta)\) by \(+1\%\) for the RASSD theory and by \(+3\%\) for the ECS theory leads to agreement with experiment. We mention this fact because the uncertainty in the determination of \((1 + \delta)\) is at least 1 to 2\%. Furthermore, this adjustment clearly shows the sensitivity of the phenomenon to the molecular parameters (one observes, for instance, an inversion of the sign of the excess viscosity calculated from the RASSD theory). There exists a similar sensitivity with respect to the molecular masses (see, for instance, the cases Ar/CH\(_4\) and Kr/CH\(_4\)).

In the case of the thermal conductivity, the discrepancies between the data of Hamman \([4-64]\) and recent measurements are most probably
explainable by the observation that Hamman did not account for the possibility of convection in his experimental apparatus [4-160]. His results are, therefore, all shifted on the temperature scale. Nevertheless, we can make use of these data when considering the relative deviations from the ideal mixture, as also calculated from Hamman's data. It is
FIG. 6. (a) Excess fluidity of the argon-methane system (91°K); experimental data [4-14]. (b) Excess viscosity of the argon-methane system (91°K); experimental data [4-14].
FIG. 7. (a) Excess fluidity of the krypton-methane system (116°C); experimental data [4-14]. (b) Excess viscosity of the krypton-methane system (116°C); experimental data [4-14].
found that agreement is obtained between the RASSD theory and experiment (see Fig. 12).

It seems rather difficult to derive any more general conclusion from this analysis than to simply point out that the RASSD theory in general appears to be more nearly correct (or at least less incorrect) as a representation of the experimental data and, consequently, that the additivity of the fluidities (ECS) may be considered to be a doubtful basic assumption.

3.4. "Complex" Liquids

In this subsection we attempt to illustrate the few remarks made in Section 2.6 with two particular examples: the shear viscosity of the isotopic pairs hydrogen and deuterium, and methane and deuteromethane. From experimental data, one observes differences in the
Fig. 9. (a) Excess fluidity of the argon-oxygen system (84°K); experimental data I-shaped [4-47], branched [4-144, 4-145]. (b) Excess viscosity of the argon-oxygen system (84°K); experimental data same as (a).

Fig. 10. (a) Excess fluidity of the nitrogen-carbon monoxide system (90.1°K); experimental data [4-59]. (b) Excess viscosity of the nitrogen-carbon monoxide system (90.1°K); experimental data [4-59].

Fig. 11. (a) Excess fluidity of the nitrogen-oxygen system (68.25°K); experimental data [4-53]. (b) Excess viscosity of the nitrogen-oxygen system (68.25°K); experimental data [4-53].
behavior of the isotopes of each pair which cannot be fully explained by the differences between the masses. The available data for the viscosity coefficients of hydrogen and deuterium are reproduced in Fig. 13. A small discrepancy (of about 10%) exists between the results of different laboratories. These deviations might arise from the use of different methods of measurement, since there remains a small uncertainty in the exact expression for the product $\eta \rho m$ in the evaluation of the viscosity from the damping of oscillations [2] because of edge effects. Indeed, van Itterbeek and van Paemel [4-163], using the oscillating disk method, obtain results for the viscosity of liquid deuterium which are 10% higher than those of Rudenko and Konareva [4-139] who made use of

![Diagram](image-url)

**Fig. 12.** Excess thermal conductivity of the nitrogen-oxygen system (70°K); experimental data [4-64].

**Fig. 13.** The coefficient of shear viscosity of hydrogen and deuterium as a function of the temperature: (○) Verschaffelt and Nicaise [4-170], (□) Keesom and MacWood [4-83], (○) Johns [4-79], (△) van Itterbeek and van Paemel [4-163], (△) van Itterbeek *et al.* [4-166], and (●) Rudenko and Konareva [4-139].
the capillary flow technique. For the viscosity of hydrogen, the values of Keesom and MacWood [4-83], obtained by the oscillating disk method, similarly deviate from the concordant results of Rudenko and Konareva [4-139] and of Johns [4-79], both of whom used capillary methods. However, the latter data are in very good agreement with the data of van Itterbeek et al. [4-166], who used the oscillating disk method. These small discrepancies thus do not seem to arise from the experimental techniques used, and may be considered negligible for the following discussion.

To a good approximation, the experimental results yield the ratio

\[ \frac{\eta_{D_2}}{\eta_{H_2}} = 3 \]  

(124)

which implies a difference of a factor of about 2 between the ratio of the viscosities and the ratio of the square roots of the masses.

Now, at the same reduced temperature, one has

\[ \frac{\eta_{D_2}(T_{D_2})}{\eta_{H_2}(T_{H_2})} = \frac{\eta^*_{D_2}}{\eta^*_{H_2}} \frac{z_{D_2}}{z_{H_2}} \]  

(125)

From the values given in Table XV,

\[ \frac{z_{D_2}}{z_{H_2}} = \left( \frac{m_{D_2}}{m_{H_2}} \right)^{1/2} \frac{(1 + \delta)^{1/2}}{(1 + \rho)^{1/2}} \simeq \left( \frac{m_{D_2}}{m_{H_2}} \right)^{1/2} \simeq 1.4 \]  

(126)

### TABLE XV

**Reduced Viscosities of Some Simple Liquids**

<table>
<thead>
<tr>
<th>(T^* = 0.555)</th>
<th>(A^*) [3]</th>
<th>(\epsilon/k) (°K)</th>
<th>Ref.</th>
<th>(\sigma(A))</th>
<th>Ref.</th>
<th>(M) (gm/mole)</th>
<th>(\ln \eta^*)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>1.729</td>
<td>36.7</td>
<td>[14]</td>
<td>2.96</td>
<td>[14]</td>
<td>2.016</td>
<td>-0.17083</td>
<td>[4-167, 166]</td>
</tr>
<tr>
<td>D(_2)</td>
<td>1.223</td>
<td>35.2</td>
<td>[14]</td>
<td>2.95</td>
<td>[14]</td>
<td>4.032</td>
<td>+0.78058</td>
<td>[4-167, 163]</td>
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<tr>
<td>Ne</td>
<td>0.593</td>
<td>35.6</td>
<td>[13]</td>
<td>2.75</td>
<td>[13]</td>
<td>20.183</td>
<td>+1.41022</td>
<td>[4-49, 75]</td>
</tr>
<tr>
<td>CD(_4)</td>
<td>0.214</td>
<td>144.6</td>
<td>[15]</td>
<td>2.92</td>
<td>[15]</td>
<td>20.074</td>
<td>+1.57246</td>
<td>[4-13]</td>
</tr>
<tr>
<td>Kr</td>
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<td>171.0</td>
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<td>3.60</td>
<td>[16]</td>
<td>83.7</td>
<td>+1.77707</td>
<td>[4-15]</td>
</tr>
<tr>
<td>Xe</td>
<td>0.064</td>
<td>236.6</td>
<td>[16]</td>
<td>3.92</td>
<td>[16]</td>
<td>131.3</td>
<td>+1.85713</td>
<td>[4-88]</td>
</tr>
</tbody>
</table>

\( \eta^* \) has been calculated from the viscosities referred to in this column using the molecular parameters given in columns 3 and 5. The value of the viscosity of liquid Ne has been adjusted to the reduced temperature \( T^* = 0.555 \).
and from (115)*

\[
\frac{\eta^*(A_{D_2}^{*2})}{\eta^*(A_{H_2}^{*2})} = \frac{1}{1 + \Delta A^{*2} \left( \frac{\partial \ln \eta^*}{\partial A^{*2}} \right) A_{D_2}^*} 
\]

(127)

with

\[
\Delta A^{*2} = A_{H_2}^{*2} - A_{D_2}^{*2} = 1.5 
\]

It is now necessary to evaluate the factor \( \left( \frac{\partial \ln \eta^*}{\partial A^{*2}} \right) \) graphically from Fig. 14. We note a decrease of the slope of the function

\[\ln \eta^* = F(A^{*2})\]

when passing from the classical region (Ar, Kr, and Xe) to the quantum mechanical domain. Near the value of \( A_{D_2}^* \), one can assume that the tangent has an absolute value intermediate between the minimum (zero) and the maximum (0.7). Taking the mean value, we obtain in first approximation:

\[
\frac{\eta^*(A_{D_2}^{*2})}{\eta^*(A_{H_2}^{*2})} \approx 2 
\]

(128)

which corresponds quite well with the ratio obtained from experiment.†

We now consider the case of the methane isotopes. The viscosities of CH\(_4\) and CD\(_4\) have been measured by Bresler and Landerman [4-18] at one temperature (90.1°K) and by Boon and Thomaes [4-13] from 91° to 115°K, both groups using the capillary flow technique. Though

* Some considerations on the application of the quantum mechanical principle of corresponding states to the transport properties of liquid He, H\(_2\), D\(_2\), T\(_2\), and Ne have been published by Kerrisk et al. [4-84], but no real interpretation of the quantum effects can be derived from their analysis.

† According to the rough sphere model no correction arises from the internal degrees of freedom when the ratio \( \eta_{D_2}/\eta_{H_2} \) is considered since, from (116), \( K_{D_2} = K_{H_2} \).
the data of Boon and Thomaes are given for the kinematic viscosities \( \nu = \eta / \rho_m \), one can easily compare their results with the one datum of Bresler and Landerman by considering the following ratio:

\[
\frac{\eta_i / \eta}{\nu_i / \nu} = \frac{m_i}{m} = 1.25
\]

(129)

where the subscript \( i \) refers to the substituted molecule (CD\(_4\)). At 90.1\(^\circ\)K, one finds from [4-13, 4-18] the ratio 1.21, which shows that the measurements are in fairly good agreement with each other if one takes into account the experimental error (which is about 1\%). In (129), the assumption was made that the molecular parameters are not affected by isotopic substitution. Therefore, Bresler and Landerman concluded from their measurement that the predicted ratio

\[
\eta_i / \eta = (m_i / m)^{1/2}
\]

(130)

was experimentally verified, while it is not by the value obtained from the experiments of Boon and Thomaes when the equivalent relation is considered:

\[
\nu_i / \nu = (m_i / m)^{1/2}
\]

(131)

The observed values at 90.1\(^\circ\)K are the following:

\[
\frac{\eta_{\text{CD}_4}}{\eta_{\text{CH}_4}} = 1.113 \quad \text{(from Bresler and Landerman [4-18])}
\]

\[
\frac{\nu_{\text{CH}_4}}{\nu_{\text{CD}_4}} = 1.088 \quad \text{(from Boon and Thomaes [4-13])}
\]

(132)

to be compared with \((m_{\text{CD}_4} / m_{\text{CH}_4})^{1/2} = 1.119\). But, since we are dealing with very small effects when considering an isotopic pair such as this, it is necessary to use great care in interpreting the observations. Indeed, it will be seen in the following discussion that the preceding (rough) remarks are erroneous and without real significance. First, we note that it has been shown, from differential measurements of the molar volumes [18] and of the second virial coefficients [15], that the intermolecular energy and the molecular diameter of CD\(_4\) are slightly smaller than the corresponding values for CH\(_4\):

\[
1 + \delta = 0.991 \quad \text{and} \quad 1 + \rho = 0.996^* 
\]

(133)

* We have chosen the value of \((1 + \delta)\) obtained from the virial coefficients since the precision of this determination is better than the corresponding evaluation from the molar volume measurements. For the same reason, the value of \((1 + \rho)\) was taken from the molar volume data.
From the data on the molar volumes \[18\] we have been able to calculate the absolute values of the viscosity coefficients from the results of Boon and Thomaes*; for instance,

\[ \eta_{\text{CH}_4} = 150.6 \times 10^{-5} \text{ poise at } 100^\circ\text{K} \]
\[ \eta_{\text{CD}_4} = 178.5 \times 10^{-5} \text{ poise at } 99.1^\circ\text{K} \]

A second difference between the isotopes which must be considered in our discussion arises from the values of their reduced wavelengths, which (slightly, but significantly) differ from one another (see Table XV). This leads to a correction of about 1\%, using the same development as for \text{H}_2 and \text{D}_2 (127). Furthermore, despite the fact that their moments of inertia are very small, one knows that \( I \) is a factor of 2 larger for the heavy molecule, i.e.,

\[ \frac{K_{\text{CD}_4}}{K_{\text{CH}_4}} = \frac{I_{\text{CD}_4}/m_{\text{CD}_4}}{I_{\text{CH}_4}/m_{\text{CH}_4}} \approx 1.6 \]

Although it is certainly a very crude approximation to consider the methane molecule to be a simple rough sphere, we obtain from the Valleau expression (116) a supplementary correction of 1\%. Combining all the preceding factors, we now obtain the following relation from the theorem of corresponding states:

\[ \frac{\eta_i(T_i)}{\eta(T)} = \left( \frac{m_i}{m} \right)^{1/2} \frac{(1 + \delta)^{1/2}}{(1 + \rho)^2} \frac{\eta^*(A_i^{1/2})}{\eta^*(A^{1/2})} \frac{[1 + (7/16) K_i][1 + (4/16) K_i]}{[1 + (7/16) K][1 + (4/16) K]} \]

which yields the value

\[ \left( \frac{\eta_i(T_i)}{\eta(T)} \right)_{\text{calc}} = 1.146 \]

to be compared with the experimental ratio obtained from (134):

\[ \left( \frac{\eta_i(T_i)}{\eta(T)} \right)_{\text{obs}} = 1.186 \]

There is no doubt that the particularly good agreement between observation and calculation for the isotope effect in liquid hydrogen and

* The datum published by Bresler and Landerman is restricted to the ratio given above.
† This corrected temperature: \( T_{\text{CD}_4} = T_{\text{CH}_4}(1 + \delta) \) corresponds to the same reduced temperature for both isotopes.
deuturium is partially fortuitous. Indeed, one should not expect significant quantitative agreement between theory and experiment from a simple phenomenological analysis. For the same reason no real significance must be attributed to the quantitative result obtained from the correction factors introduced into the interpretation of the viscosities of the methane isotopes. Nevertheless, in both cases, given our present ignorance of the nature of complex fluids, the encouraging fact is that the introduction of the elements relevant to quantum effects and to internal degrees of freedom permits us to obtain, at least qualitatively, valuable information. Furthermore, we wish to mention the availability of data concerning the mixtures CH₄/CD₄ [4-47], whose viscosity is almost that of an ideal mixture; the differences in the transport coefficients (κ and η) of normal and parahydrogen and of normal and orthodeuterium have also been measured [4-7, 66, 124–126, 138, 140, 172, 173], but at the present time our theoretical background does not permit any plausible interpretation of the observed deviations.

REFERENCES


* For instance, a similar development for the neon-deuterium pair, which can be considered in a certain sense to be "isotopic species" (see Table XV), leads to the correct qualitative result, but with a discrepancy of about 30% between theory and experiment.
† The same kind of calculation performed for the case of the thermal conductivity would lead to equivalent conclusions.
‡ This system was examined from a classical point of view in Section 3.3.

## 4. Literature Survey

This section is devoted to a bibliography of references concerned with the viscosity, thermal conductivity, self-diffusion, and ionic mobility in hydrogen, deuterium, neon, argon, krypton, xenon, carbon monoxide, oxygen, nitrogen, methane, and deuteromethane, and some of their mixtures in the liquid phase. This survey, based on a literature search made for us by the National Bureau of Standards, was completed in 1965. Our aim has been to give the literature that has been brought to our attention, as of the date cited, as exhaustively as possible. A bibliography supplement at the end of this chapter (Section 4.2) extends the survey up to November 1966. However, these recent references were added later and are therefore not included in the following classification.

Tables XVI to XX display a classification of the above properties, substance by substance, for all the substances considered; the numbers in column two refer to the alphabetical list of references in Section 4.1. This bibliography includes articles, reports, reviews, and books containing original experimental results (denoted by E in the tables); theoretical or empirical interpretations, calculations or predictions of the above properties (denoted by T); and compilations, and surveys as well as simple reproductions of data (denoted by C).

In the Bibliography of References, the citations are arranged alphabetically by first author’s name and then numbered; the information given for each reference includes:

- Author(s) names(s);
- Title of the article (original language) and the translated title, if the original is other than English;
- Original reference, if the citation refers to an English translation; Chemical Abstract number and/or Armed Forces Technical Information Agency (ASTIA) number, when these are known;
- Information on figures, tables, references, etc., given in the article;
- Substances considered and the properties studied, the state(s) of the substances, etc.

Further information is also given according to the following characteristic coding designations (NBS code):
**Categories**

A1: Books, reviews, surveys, bibliographies, proceedings, etc.
A2: Properties of solids
A3: Properties of fluids
A4: Solid state, theoretical, phenomena, basic physics, etc.
A5: Cryogenic techniques, tricks, unique methods, unusual procedures, etc.
A6: Cryogenic processes, heat transfer, purification, fluid flow, liquefaction, safety procedures, etc.
A7: Laboratory equipment and instrumentation
A8: Cryogenic equipment
A9: General interest literature, news, management, programs, accidents, miscellaneous

**Language**

B1: English; B2: French; B3: German; B4: Dutch; B5: Italian; B6: Japanese; B7: Russian; B8: Spanish; B9: Other

**Cryogenic Interest**

C1: Cryogenic temperature range (0° to 130°K where not specifically designated in C4 through C7 below)
C2: Cryogenic interest but not in cryogenic temperature range (except where designated C8)
C3: Not of direct cryogenic interest
C4: Below 1°K
C5: 1° to 10°K
C6: 10° to 50°K
C7: 50° to 130°K
C8: 130° to 300°K

**Form of Data (omitted where not pertinent)**

D1: Numerical data included
D2: No data
D3: Graphical data only

**Type of Article (omitted where not pertinent)**

E1: Experimental, experimental and theoretical, original work
E2: Review article, compilation, correlation, discussion
E3: Theoretical only, no specific data given

**Availability of Document (suggested source)**

F1: Cryogenic Engineering Laboratory
F2: National Bureau of Standards (NBS)
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^a Normal and parahydrogen.
^b Normal and orthodeuterium.
^c Ozone.
### TABLE XIX

**Self-Diffusion $D$**

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<th>Authors</th>
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<th>$H_2$</th>
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* Positive ions.

* Negative ions.
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   conductivity, viscosity, specific heat, velocity of sound, heat of vaporization, dielectric
   constant, vapor pressure, surface tension

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   Viscosity, hydrocarbon, gaseous, methane, ethane, propane, butane, liquid

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viscosity, hydrocarbon, argon, organic fluid, methane carbon tetrachloride, benzene, electric field, melting point, organic halide, halogen, sodium, potassium, tin, mercury, lead, copper, chloride, cesium, bromide, liquid

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viscosity, liquid, hydrogen, deuterium, neon, argon, krypton, carbon monoxide, nitrogen, oxygen, methane, deuteromethane, liquid mixtures

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The fluidity of binary mixtures.  
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rare gas, krypton, argon, liquid mixtures, binary system, viscosity

13. J. P. Boon and G. Thomas  
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A3 B1 C7 D1 E1 F6 G1  
deuteromethane, deuterocompound, viscosity, liquid, saturated liquid

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binary system, viscosity, liquid mixture, argon, methane, krypton, rare gas

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viscosity, liquid, argon, oxygen, methane, krypton, rare gas

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liquid, thermal conductivity, water, nitrogen, theory

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Thermal conductivity of liquid nitrogen, carbon monoxide, methane, and ethylene.  
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nitrogen, liquid, carbon monoxide, methane, ethylene, temperature effect, thermal conductivity

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The viscosity of CH₄ and CD₄.  
A3 B7 C7 D1 E1 F6 G1  
viscosity, liquid methane, deuteromethane, rare gas

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Thermodynamic data on oxygen and nitrogen.  
A3 B1 C7 D1 E2 F8 G5
oxygen, air, nitrogen, gaseous, liquid, viscosity, thermal conductivity, density, transport property, Prandtl number, saturated liquid, compilation, bibliography, temperature effect, gaseous mixture, liquid mixture, phase equilibrium, dew point, bubble point, concentration effect, binary system

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hydrogen, deuterium, liquid, viscosity, temperature effect

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A3 B3 C8 D1 E1 F7 G1
thermal conductivity, krypton, argon, neon, helium, hydrogen, methane, nitrogen, carbon monoxide, oxygen, gaseous, carbon dioxide, oxide of nitrogen

22. R. V. Burry, J. Jortner, and J. K. Rosemary
High energy propellant comparisons for space missions.
A6 B1 C7 D1 E2 F6 G1 61
heat transfer, cryogenic fluid, space application, radiation, thermal radiation;
A3 B1 C7 D1 E2
propellant, gaseous mixture, fluorine, hydrogen, oxygen, hydrazine, binary system, thermal conductivity, organic fluid, space application

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A3 B1 C7 D E1 F5 G5
oxygen, liquid, gaseous, thermal conductivity, temperature effect

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nitrogen, argon, gaseous, liquid, thermal conductivity

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hydrogen, slush, production, fluid transfer, storage, mechanical property, gas injection, helium;
A3 B1 C6 D3 E1
hydrogen, vapor pressure, liquid, solidified gas, viscosity, mechanical property, slush

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A3 B1 C5 D1 E2 F8 G2 56
liquid, gaseous, hydrogen, nitrogen, helium, deuterium, heat of vaporization, density, vapor pressure, entropy, enthalpy, T-S diagram;
A3 B1 C5 D1 E2
hydrogen, helium, deuterium, liquid, gaseous, viscosity, specific heat, surface tension, dielectric constant, thermal conductivity;
A3 B1 C5 D1 E2
air, heat of vaporization, melting curve, oxygen, density, liquid.

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ASTIA AD 208 155
A3 B1 C5 D1 E2 F5 G2
liquid, gaseous, nitrogen, helium, deuterium, heat of vaporization, density, vapor pressure, entropy, enthalpy, T-S diagram, hydrogen, viscosity, specific heat, surface tension, dielectric constant, thermal conductivity, air, melting curve, oxygen, aluminum, stainless steel, glass, copper, lead, iron, steel, thermal expansion, alloy, beryllium copper, Everdur, phosphorbronze, tensile property, Monel, notch property, insulation, polystyrene, Santocel, Teflon, nylon, thermoelectricity, thermoelectric emf, Copper Constantan, gold cobalt

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Self-diffusion of carbon monoxide in liquid phase.
A3 B1 C7 D1 E1 F6 G1 64
carbon monoxide, liquid, transport property, diffusion coefficient, self-diffusion, law of corresponding states;
A3 B1 C7 D3 E2
transport property, self-diffusion, argon, krypton, methane

29. G. Cini-Castagnoli and F. P. Ricci
Self-diffusion in liquid argon.
A3 B1 C7 D1 E1 F6 G1 60
argon, liquid, transport property, diffusion coefficient, self-diffusion

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Transport properties in the liquid state and the corresponding state principle.
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argon, oxygen, carbon monoxide, nitrogen, methane, liquid, viscosity, thermal conductivity, temperature effect, reduced variable, law of corresponding states

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CA 49 539f
A3 B2 C8 D1 E2 F7 G1 53
hydrocarbon, heptane, pentane, gaseous, viscosity, thermal conductivity, ethane,
transport property, Prandtl number;
A3 B2 C8 D1 E2
helium, hydrogen, air, nitrogen, oxygen, carbon dioxide, water, ammonia, methane,
gaseous, viscosity, thermal conductivity, transport property, Prandtl number

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potential.
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A3 B1 C7 D1 E3 F7 G1
viscosity, thermal conductivity, self-diffusion, liquid, argon
(b) I. McLaughlin and H. T. Davis
Transport properties of a dense binary mixture of molecules interacting with a square-well potential.
A3 B1 C7 C8 D2 E3 F7 G1
viscosity, thermal conductivity, self-diffusion, thermal diffusion, mutual diffusion, liquid

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On the kinetic theory of simple dense fluids. XI. Experimental and theoretical studies of positive ion mobility in liquid argon, krypton and xenon.
A3 B1 C7 D1 E1 F7 G1
mobility, liquid, argon, krypton, xenon

On the kinetic theory of simple dense fluids. XIII. The mobility of negative ions in liquid argon, krypton and xenon.
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mobility, liquid, argon, krypton, xenon.

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viscosity, liquid, hydrogen

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oxygen, liquid, purification, space application, solubility, contamination, vapor pressure, nitrogen, argon, methane, krypton, rare gas, inorganic fluid, oxide of nitrogen, ethylene, ethane, acetylene, carbon dioxide, density, hydrogen, helium, nitrogen, carbon monoxide, thermal conductivity, gaseous, neon, water, dew point, solidified gas, acetone, ammonia

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Significant structure theory of liquids.
CA 60 1132g
A3 B1 C1 D1 E3 F6 G1 63
liquid, argon, nitrogen, methane, surface tension, viscosity, theory;
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hydrogen, normal hydrogen, parahydrogen, hydrogen deuteride, deuterium, liquid, density, triple point, boiling point, critical constant, vapor pressure, thermodynamic property

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self-diffusion, liquid, rare gases

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A3 B3 C7 D1 E1 F7 G1 42
nitrogen, liquid, viscosity

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Viscosity of liquefied pure gases and their mixtures, II.
A3 B7 C7 D1 E1 F7 G1 41
oxygen, ethane, propane, hydrocarbon, liquid, coefficient, propene, viscosity, temperature effect;
A3 B7 C7 D1 E1
liquid mixture, ethane, propene, hydrocarbon, viscosity, concentration effect, temperature effect, binary system;
A3 B7 C7 D1 E1
liquid mixture, oxygen, nitrogen, viscosity, concentration effect, temperature effect, binary system

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Sound absorption and velocity in liquefied argon, oxygen, nitrogen, and hydrogen.
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sound attenuation, liquid hydrogen, nitrogen, oxygen, argon

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Self-diffusion and impurity-controlled proton relaxation in liquid methane.
A3 B1 C7 D3 E1 F6 G1 63
methane, liquid, transport property, self-diffusion, activation energy

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Properties of selected rocket propellants.
DDC AD 450 926
A3 B1 C1 D1 E2 F5 G5 63
hydrogen, liquid, gaseous, density, thermal conductivity, viscosity, vapor pressure, enthalpy, specific heat, oxygen, surface tension, velocity of sound, heat of vaporization;
A3 B1 C1 D1 E2
hydrogen, liquid, dielectric constant, entropy, compressibility factor, compatibility;
A3 B1 C1 D1 E2
oxygen difluoride, liquid, vapor pressure, density, viscosity;
A3 B1 C1 D1 E2
oxygen difluoride, gaseous, specific heat, entropy, enthalpy, free energy;
A3 B1 C1 D1 E2
oxygen, compressibility, liquid, compatibility;
A6 B1 C1 D1 E2
TRANSPORT PHENOMENA IN SIMPLE LIQUIDS

hydrogen, oxygen, oxygen difluoride, handling, safety, production, storage, liquid, fluorine;
A3 B1 C1 D1 E2

Fluorine, density, liquid, vapor pressure, viscosity, surface tension, heat of vaporization, specific heat, enthalpy, entropy, compatibility

57. H. George
Properties of selected propellants. Volume I.
A3 B1 C1 D1 E2 F5 G5 63

fluorine, corrosion, liquid, density, vapor pressure, viscosity, surface tension, solidified gas, enthalpy, entropy, specific heat, heat of vaporization, heat of fusion, saturated liquid;
A3 B1 C1 D1 E2

fluorine, gaseous, density, viscosity, entropy, thermal conductivity, enthalpy, saturated vapor, specific heat, free energy, Mollier diagram, dielectric constant;
A3 B1 C1 D1 E2

hydrogen, gaseous, liquid, density, viscosity, thermal conductivity, specific heat, vapor pressure, surface tension, velocity of sound, heat of vaporization, dielectric constant, compatibility, enthalpy;
A3 B1 C1 D1 E2

oxygen, liquid, density, compressibility, viscosity, thermal conductivity, heat of vaporization, specific heat, enthalpy, vapor pressure, surface tension, velocity of sound, specific heat ratio;
A3 B1 C1 D1 E2

oxygen difluoride, liquid, vapor pressure, density, viscosity, gaseous, specific heat, entropy, enthalpy, free energy, heat of vaporization;
A6 B1 C1 D1 E2

fluorine, hydrogen, oxygen difluoride, handling, storage, transportation, safety, production, decontamination, explosion, fire hazard

58. S. F. Gerf and G. I. Galkov
Viscosity of liquefield pure gases and their mixtures, I.
A3 B7 C7 D1 E1 F7 G1

viscosity, binary system, liquid, nitrogen, ethane, methane, liquid mixture, ethylene, propane, propene

59. S. F. Gerf and G. I. Galkov
Viscosity of liquefied pure gases and their mixtures, III.
A3 B7 C7 D1 E1 F7 G1 41

viscosity, liquid, ethane, carbon monoxide, methane, ethylene;
A3 B7 C7 D1 E1

viscosity, liquid mixture, binary system, methane, nitrogen;
A3 B7 C7 D1 E1

methane, ethylene, liquid mixture, binary system, viscosity;
A3 B7 C7 D1 E1

carbon monoxide, nitrogen, liquid mixture, binary system, viscosity

60. P. Grassmann
Elektrische verfahren zur messung von warme- und stoffaustausch. (Electrical methods for measuring heat and mass transfer.)
382 STUART A. RICE, JEAN PIERRE BOON, AND H. TED DAVIS

A7 B3 C8 D3 E2 F7 G1 63
measurement, electrical equipment, thermal property, thermal conductivity, diffusion coefficient, gaseous, liquid;
A3 B3 C8 D3 E2
nitrogen, gaseous, thermal conductivity, pressure effect

61. P. Gray and S. A. Rice
On the kinetic theory of dense fluids. XVIII. The bulk viscosity.
A3 B1 C3 D2 E3 F6 G1
viscosity, liquid

62. J. Grey
The turbine flow meter for cryogenic liquids.
8 pp., 8 fig., 1 tab.
A7 B1 C1 D E F8 G9
viscosity, liquid, helium, hydrogen, nitrogen, oxygen

63. L. A. Hall, J. G. Hust, and A. L. Gosman
A bibliography of thermophysical properties of argon from 0 to 300°K.
A3 B1 C7 D2 E2 F4 G6 64
argon, solidified gas, liquid, gaseous, bibliography, annotated bibliography

64. G. Hamman
Wärmeleitfähigkeit von flussigem Sauerstoff, flussigem stickstoff und ihren Gemischen.
(Thermal conductivity of liquid oxygen and liquid nitrogen and their mixtures.)
CA 32 8907
A3 B3 C1 D1 E1 F7 G1
oxygen, nitrogen, liquid, liquid mixture, binary system, thermal conductivity, temperature effect

65. D. J. Harrison
The viscosity of hydrogen.
DDC AD 434 141
A3 B1 C6 D1 E2 F5 G5 64
hydrogen, gaseous, liquid, viscosity, temperature effect, pressure effect

66. K. Heinzinger, W. Eichenauer, and A. Klemm
Die warmeleitfähigkeiten von normal und ortho-deuterium bei temperaturen des flussigen wasserstoffes. (Thermal conductivity of normal and orthodeuterium at liquid hydrogen temperatures.)
CA 59 5801b
A3 B3 C6 D3 E1 F7 G1 63
deuterium, orthoparadeuterium, gaseous, thermal conductivity, orthodeuterium

67. B. L. Henson
Mobility of positive ions in liquefied argon and nitrogen.
A3 B1 C7 D1 E1 F7 G1
mobility, liquid, argon, nitrogen
68. C. K. Hersh
Production and properties of liquid ozone and liquid ozone-oxygen mixtures, a review.
A3 B1 C7 D1 E2 F6 G2
oxygen, ozone, liquid mixture, liquid, phase transition property, critical constant, thermal conductivity, heat of vaporization, binary system, surface tension, viscosity, density.

69. C. K. Hersh, A. W. Berger, and J. R. C. Brown
Physical properties of liquid ozone-oxygen mixtures.
Density viscosity, and surface tension.
CA 54 2858i
A3 B1 C7 D1 E1 F6 G1
liquid mixture, oxygen, ozone, density, viscosity, surface tension, concentration effect, liquid

70. F. K. Heumann
Analysis of hydrogen-tritium mixtures by the thermal conductivity method.
A3 B1 C2 D1 E1 F8 G5
hydrogen, tritium, mixture, thermal conductivity

71. J. K. Horrocks and E. McLaughlin
Thermal conductivity of simple molecules in the condensed state.
A3 B1 C7 D1 E3 F7 G1 60
argon, nitrogen, carbon monoxide, methane, organic fluid, benzene, carbon tetrachloride, inorganic fluid, liquid, thermal conductivity, equation, calculation

72. J. K. Horrocks and I. McLaughlin
Temperature dependence of the thermal conductivity of liquids.
C1 59 9344g
A3 B1 C1 D E3 F7 G1 63
thermal conductivity, liquid, carbon monoxide, argon, nitrogen, methane, temperature effect

A bibliography of the thermophysical properties of oxygen at low temperatures.
A3 B1 C6 D2 E2 F3 G6
oxygen, PVT data, compressibility, liquid, expansivity, equation of state, virial coefficient, specific heat, velocity of sound, vapor pressure, critical constants, phase transition property, gaseous, solidified gas, entropy, enthalpy, free energy, thermal conductivity, viscosity, transport property, Prandtl number, diffusion coefficients, Joule-Thomson coefficient, density, melting curve, triple point, solid-solid transition, heat of fusion, heat of sublimation, heat of vaporization, thermal expansion

74. G. W. Hutchinson
Ionization in liquid and solid argon.
Nature 162, No. 4120 (1948).
A1 B1 C7 D1 E1 F7 G1
mobility, liquid, solid, argon
75. F. Huth
The viscosity of liquid neon.
*Cryogenics* 2, 368 (1962). 1 fig., 4 ref.
A3 B1 C6 D3 E1 F7 G1
neon, liquid, viscosity, boiling-to-critical point

76. L. D. Ikenberry
Thermal conductance in simple liquids.
A3 B1 C7 D1 E1 F9 G7
thermal conductivity, liquid, argon, krypton, xenon, methane

77. L. D. Ikenberry and S. A. Rice
Kinetic theory of dense fluids. XIV. Experimental and theoretical studies of thermal
conductivity in liquid Ar, Kr, Xe, and CH₄.
CA 59 8136b
A3 B1 C7 D E1 F6 G1 63
thermal conductivity, methane, argon, krypton, xenon, rare gas, liquid, transport
property, self-diffusion

78. A. C. Jenkins and F. S. DiPaolo
Some physical properties of pure liquid ozone and ozone-oxygen mixtures.
A3 B1 C1 D1 E1 F6 G1
ozone, liquid, viscosity, melting point, surface tension, mixture, oxygen

79. H. E. Johns
The viscosity of liquid hydrogen.
A3 B1 C1 D1 E1 F7 G1
hydrogen, liquid, viscosity, capillary

80. V. J. Johnson, ed.
A compendium of the properties of materials at low temperature (Phase I). Part I.
Properties of fluids.
A3 B1 C5 D1 E2 F1 G6
carbon monoxide, hydrogen, neon, nitrogen, fluorine, methane, oxygen, air, helium,
argon, vapor pressure, thermal conductivity, dielectric constant, surface tension,
phase transition property, viscosity, specific heat, density, enthalpy, expansivity

81. J. A. Jossi, L. I. Stiel, and G. Thodos
The viscosity of pure substances in the dense gaseous and liquid phases
A3 B1 C1 D3 E3 F6 G1
gaseous, liquid, viscosity, calculation, argon, nitrogen, oxygen, carbon dioxide,
methane, ethane, propane, butane, pentane, sulfur dioxide

82. M. Kh. Karapet’yants, and K.-S. Yen
Temperature dependence of viscosity of n-alkanes.
CA 59 13369e
A3 B7 C7 D3 E2 F7 G1 63
methane, ethane, propane, butane, hydrocarbon, pentane, heptane, paraffin class,
liquid, viscosity, temperature effect, equation, calculation
83. W. H. Keesom and G. E. MacWood
The viscosity of liquid hydrogen.
A3 B1 C1 D1 E1 F6 G1
viscosity, liquid, hydrogen

84. J. F. Kerrisk, J. D. Rogers, and E. F. Hammel
Transport properties of He₃, He₄, H₂, D₂, T₂, and Ne in the liquid state according to the quantum mechanical principle of corresponding states.
A3 B1 C5 D1 E3 F6 G2 64
thermal conductivity, viscosity, helium, helium-4, hydrogen, deuterium, tritium, neon, law of corresponding states, liquid, reduced variable, quantum effect, Lennard-Jones function

85. F. G. Keyes
The heat conductivity, viscosity, specific heat and Prandtl numbers for thirteen gases.
ASTIA ATI-167-173
A3 B1 C1 D1 E2 F5 G6
viscosity, thermal conductivity, air, CH₄, O₂, H₂, N₂, CO, He

86. F. G. Keyes
The thermal conductivity of gases.
CA 50, 635D
A1 B1 C8 D1 E2 F6 G1
thermal conductivity, liquid, gas 87° to 273°K, 1 to 11 atm, N₂, O₂, CH₄, Xe, Kr, CO

87. J. G. Kirkwood, F. P. Buff, and M. S. Green
The statistical mechanical theory of transport processes. III. The coefficients of shear and bulk viscosity of liquids.
A3 B1 C7 D1 E3 F6 G1 49
argon, liquid, viscosity

88. J. C. Legros and G. Thomaes
The viscosity of liquid xenon.
A3 B1 C7 D1 E1 F6 G1
viscosity, liquid, xenon, rare gas

89. D. A. Lennert and G. Thodos
Application of Enskog relationships for prediction of the transport properties of simple substances.
A3 B1 C1 D1 E3 F8 G9 63
viscosity, thermal conductivity, transport property, thermal diffusivity, equation, pressure effect, gaseous, liquid, argon, krypton, nitrogen, oxygen, Enskog formula

90. P. E. Liley
Survey of recent work on the viscosity, thermal conductivity, and diffusion of gases and liquefied gases below 500°K.
A3 B1 C1 D2 E2 F8 G5
viscosity, thermal conductivity, diffusion, technical gas, inert gas, oxide of nitrogen, fluorinated refrigerant, methane, ethane, deuterium, hydrocarbon, liquid, mixture, bibliography, properties of fluids, gases, liquids

91. S. H. Lin, H. Eyring, and W. J. Davis
Thermal conductivity of liquids.
A3 B1 C7 D1 E3 F8 G9 64
thermal conductivity, argon, nitrogen, methane, liquid

92. S. H. Lin, H. Eyring, and W. J. Davis
Thermal conductivity of liquids.
A3 B1 C1 D1 E3 F6 G1 64
thermal conductivity, liquid, nitrogen, argon, methane, pressure effect, temperature effect

93. Linde Air Products Co.,
Technical data on liquid nitrogen.
A3 B1 C7 D3 E2 F8 G5 57
nitrogen, liquid gaseous, saturated liquid, saturated vapor, thermal conductivity, viscosity, thermodynamic property, Mollier diagram, superheated PVT data, enthalpy, phase diagram;
A3 B1 C7 D3 E2
nitrogen, boiling temperature, melting temperature, critical constants, heat of vaporization, gaseous, density

94. Liquid Propellant Information Agency
The handling and storage of liquid propellants (liquid propellant safety manual).
A6 B1 C1 D1 E2 F8 G5
handling, storage, hazards, liquid, oxygen, nitrogen, hydrogen, fluorine, safety, acid, ammonia, propellant, hydrogen peroxide, chemical property, vapor pressure, critical constant, viscosity, compatibility, oxide of nitrogen, alcohol, fluoride, borane, hydrazine, hydrocarbon, inorganic fluid, organic fluid

95. Liquid Propellant Information Agency
Liquid propellant manual.
A3 B1 C6 D3 E2 F8 G2
hydrogen, parahydrogen, liquid, density, vapor pressure, surface tension, viscosity, thermal conductivity, dielectric constant, heat of vaporization, specific heat, enthalpy, compatibility, evaporation rate, oxygen, compressibility, adiabatic, refractive index, specific heat ratio, fluorine, entropy, T-H diagram, safety, handling, storage, hazards, fire hazard, explosion hazards, transfer, gaseous, inorganic fluid, oxide of nitrogen, melting curve, boiling temperature, organic fluid, hydrazine, fluoride, chloride, boron hydride, solution, solubility, bromine, nitrogen trifluoride, ammonia, expansivity, thermal expansion, hydrogen peroxide, acid, nitrogen, liquid mixture, water, phase equilibrium
96. E. Löchtermann
Thermal conductivity of liquid neon.
A3 B1 C6 D1 E1 F7 G1
neon, nitrogen, liquid, thermal conductivity, argon, deuterium, hydrogen, helium, reduced variable, law of corresponding states

97. B. A. Lowry
Experimental and theoretical studies of the viscosity of liquid argon.
A3 B1 C7 D1 E1 F9 G7
viscosity, liquid, argon

98. B. A. Lowry, S. A. Rice, and P. Gray
Kinetic theory of dense fluids. XVII. The shear viscosity.
A3 B1 C7 D1 E1 F6 G1 64
argon, liquid, viscosity

99. K. D. Luks, M. Miller, and H. T. Davis
Predicted transport coefficients for a square-well fluid.
*A.I.Ch.E.* 12, 1079 (1966).
A3 B1 C7 D1 E3 F7 G1
viscosity, thermal conductivity, liquid, self-diffusion, argon, krypton, xenon

100. R. J. Lunbeck
Het principe van overeenstemmende toestanden in de quantummechanica. (The principle of corresponding states in quantum mechanics.)
A3 B4 C1 D1 E3 F9 G7
reduced variable, law of corresponding states, intermolecular force, Lennard-Jones function, helium, neon, argon, rare gas, krypton, xenon, hydrogen, deuterium, nitrogen, carbon monoxide, methane, equation of state, gaseous, second virial coefficient, third virial coefficient, viscosity, Joule-Thomson coefficient, oxygen, critical constant, triple point, hydrogen deuteride, deuterium, tritium, inorganic fluid, tritide, liquid, solidified gas, vapor pressure, isotope, helium-3

101. P. B. Macedo and T. A. Litovitz
On the relative roles of free volume and activation energy in the viscosity of liquids.
A3 B1 C7 D1 E3 F6 G1 65
viscosity, liquid, argon, pressure effect

102. J. J. Markham, R. T. Beyer, and R. B. Lindsey
Absorption of sound in fluids.
A3 B1 C1 D1 E2 F6 G1
helium, argon, hydrogen, nitrogen, oxygen, gaseous, water, carbon dioxide, viscosity, velocity of sound, sound absorption coefficient, liquid, sound absorption, organic fluid, physical property

103. I. V. Matyash, O. O. Galkin, and L. M. Tarasenko
Proton magnetic relaxation in methane.
CA 58 13325c
A3 B7 C7 D E1 F7 G1 63
methane, solidified gas, liquid, transport property, diffusion coefficient, self-diffusion

104. D. M. McCall and H. J. Pain
The thermal conductivity of liquid ortho- and para-hydrogen.
A3 B1 C6 D1 E1 F8 G5
hydrogen, liquid, thermal conductivity, pressure effect, normal

105. E. McLaughlin
Viscosity and self-diffusion in liquids.
A3 B1 C7 D1 E3 F7 G1 59
argon, nitrogen, carbon monoxide, methane, organic fluid, benzene, inorganic fluid, carbon tetrachloride, liquid, viscosity, transport property, self-diffusion, diffusion coefficient, equation

106. E. McLaughlin
The thermal conductivity of liquids and dense gases.
A3 B1 C1 D1 E2 F6 G1 64
Prandtl number, thermal conductivity, liquid, nitrogen, carbon monoxide, methane, carbon dioxide, argon;
A3 B1 C1 D1 E2
transport property, diffusion coefficient, argon, gaseous, liquid, viscosity, thermal conductivity

107. J. Naghizadeh
Self-diffusion in simple liquids.
A3 B1 C7 D1 E1 F9 G7
self-diffusion, liquid argon, krypton, xenon, methane

108. J. Naghizadeh and S. A. Rice
A3 B1 C7 D E F8 G5
argon, rare gas, krypton, xenon, methane, transport property, diffusion coefficient, self-diffusion, liquid, temperature effect, pressure effect

109. K. Namikawa and P. J. Petrozzi
Properties of nitrogen.
DDC AD 439 793
A3 B1 C7 D1 E2 F5 G5 63
nitrogen, gaseous, density, viscosity, specific heat, thermal conductivity, liquid, vapor pressure, heat of vaporization, dielectric constant, velocity of sound, compressibility, refractive index, specific heat ratio;
A3 B1 C7 D1 E2
nitrogen, solidified gas, specific heat, solid-solid transition, dielectric constant

110. W. C. Nason
Some physical properties of air and its components.
viscosity, liquid, gas 84° to 300°K, N₂, O₂, H₂, He, CO₂, air

111. D. G. Naugle

Ultrasonic attenuation in liquid argon.

112. D. G. Naugle, J. H. Lunsford, and J. R. Singer

Excess ultrasonic attenuation and intrinsic volume viscosity in liquid argon.

113. D. G. Naugle and C. F. Squire

Ultrasonic attenuation in liquid argon.

114. A. H. Nissan

Viscosity-temperature function of liquids.

115. E. N. Ovchinnikova and G. L. Kobus

Temperature dependence of the viscosity of pure liquids. I.

116. E. J. Owens

Reduced thermal conductivity correlation for the inert gases.

117. E. J. Owens and G. Thodos

Thermal-conductivity-reduced-state correlations for the inert gases.

118. E. J. Owens and G. Thodos

Reduced thermal conductivity chart for methane.
119. P. E. Parisot and E. F. Johnson
Liquid viscosity above the normal boiling point.
A3 B1 C7 D1 E1 F6 G1
hydrocarbon, methane, ethane, viscosity, propane, butane, hydrocarbon

120. N. V. Pavlovich and D. L. Timrot
An experimental study of the viscosity of methane.
A3 B1 C7 D1 E1 F7 G1
methane, viscosity, liquid, gaseous, pressure effect

121. R. W. Powers, H. L. Johnston, and R. W. Mattox
The thermal conductivity of liquid nitrogen between 65° and 90°K.
A3 B1 C7 D1 E1 F7 G2
thermal conductivity, measurement, liquid nitrogen, nitrogen, liquid, temperature effect

122. R. W. Powers, R. W. Mattox, and H. L. Johnston
The thermal conductivity of liquid nitrogen between 65° and 90°K.
ASTIA ATI 105 926
A3 B1 C7 D1 E1 F5 G5
thermal conductivity, nitrogen, liquid, temperature effect

123. R. W. Powers, R. W. Mattox, and H. L. Johnston
Thermal conductivities of condensed gases. I. The thermal conductivity of liquid nitrogen between 65° and 90°K.
CA 49 3597
A3 B1 C7 D1 E1 F6 G1
nitrogen, liquid, thermal conductivity, temperature effect, equation

124. R. W. Powers, R. W. Mattox, and H. L. Johnston
Thermal conductivity of condensed gases. II. The thermal conductivities of liquid normal and of liquid parahydrogen from 15° to 27°K.
A3 B2 C6 D1 E1 F6 G1
hydrogen, normal hydrogen, parahydrogen, liquid, thermal conductivity, temperature effect, equation

125. R. W. Powers, R. W. Mattox, and H. L. Johnston
Thermal conductivity of condensed gases. III. The thermal conductivity of liquid deuterium from 19° to 26°K.
A3 B1 C6 D1 E1 F6 G1
thermal conductivity, deuterium, liquid, equation, temperature effect

126. R. W. Powers, R. W. Mattox, and H. L. Johnston
The thermal conductivities of liquid normal and of liquid parahydrogen from 15° to 27°K.
ASTIA ATI 105 927
A3 B1 C6 D1 E1 F5 G5 hydrogen, parahydrogen, liquid, thermal conductivity, temperature effect

127. S. Prosad
Thermal conductivity of liquid nitrogen.
*Current Sci. (India)* 20, 264 (1951).
CA 46 6920h
A3 B1 C7 D1 E F7 G1 thermal conductivity, nitrogen, liquid

128. S. Prosad
Thermal conductivity of liquid oxygen.
CA 46 5949g
A3 B1 C7 D1 E1 F6 G1 thermal conductivity, liquid, oxygen, temperature effect

129a. T. S. Ree, T. Ree, and H. Eyring
Significant structure theory of transport phenomena.
C71-C78 (Preprint)
A3 B1 C7 D1 E3 F8 G9 64 viscosity, liquid argon, nitrogen, methane, chlorine, density;
A3 B1 C7 D1 E3 transport property, diffusion coefficient, liquid, argon, methane

129b. T. S. Ree, T. Ree, and H. Eyring
Significant structure theory of transport phenomena.
A3 B1 C1 D1 E3 F6 G1 64 viscosity, argon, liquid, nitrogen, methane;
A3 B1 C1 D1 E3 transport property, diffusion coefficient, liquid, argon, methane

130. S. A. Rice
Kinetic theory of simple liquids.
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A3 B1 C5 D E1 F6 G1 63 helium, neon, argon, krypton, liquid, thermal conductivity, viscosity, transport property, diffusion

131. S. A. Rice and P. Gray
A3 B1 C7 D1 E1 F7 G2 book, viscosity, thermal conductivity, self-diffusion, mobility, liquid, dense gas, thermodynamic properties.

132. L. Riedel,
Neue Warmeleitfähigkeitsmessungen an organischen Flüssigkeiten. (New thermal conductivity measurements for organic liquids.)
A3 B3 C8 D1 E1 F7 G1 liquid, thermal conductivity, organic fluid, benzene, toluene, ethyl benzene, xylene, carbon tetrachloride, organic halide, alcohol, ether, acetone, amine, reduced variable, nitrogen, oxygen, methane
133. L. Riedel
Kompressibilität, Oberflächenspannung und Wärmeleitfähigkeit im flüssigen
Zustand. Untersuchungen über eine Erweiterung des Theorems der übereinstim-
menden Zustande. Teil. IV. (Compressibility, surface tension, and thermal con-
ductivity in the liquid state. Investigation concerning an extension of the theory of

corresponding states. Part IV.)

A3 B3 C7 D3 E3 F7 G1
reduced variable, law of corresponding states, compressibility, surface tension,
liquid, nitrogen, oxygen, thermal conductivity, inorganic fluid, organic fluid

134. J. D. Rogers, K. Zeigler, and P. McWilliams
Hydrogen transport property correlations.
A3 B1 C6 D1 E3 F6 G1
hydrogen, gaseous, liquid, thermal conductivity, viscosity, density, equation,
calculation

135. J. D. Rogers, R. K. Zeigler, and P. McWilliams
Hydrogen transport property correlations. Part II.
Alamos, New Mexico, June 1962. 40 pp., 2 fig., 11 tab., 10 ref.
A3 B1 C6 D1 E3 F8 G5
hydrogen, gaseous, thermal conductivity, normal hydrogen, parahydrogen, viscosity,
liquid, calculation

136. N. S. Rudenko
The viscosity of liquid oxygen, nitrogen, methane, ethylene and air.
A3 B1 C7 D1 E1 F7 G1
viscosity, liquid, oxygen, nitrogen, methane, ethylene, air, boiling point to critical point

137. N. S. Rudenko
Molecular weight, density and viscosity of liquefied gases.
A3 B7 C1 D1 E1 F7 G1
density, viscosity, liquid, hydrogen, deuterium, methane, ethane, carbon monoxide,
nitrogen, oxygen, argon, chlorine, ethylene

138. N. S. Rudenko and V. G. Konareva
The viscosity of para- and ortho-hydrogen.
A3 B7 C6 D1 E1 F6 G1
viscosity, liquid, hydrogen

139. N. S. Rudenko and V. G. Konareva
Viscosity of liquid hydrogen and deuterium.
Russ. J. Phys. Chem. 37, 1493–1494 (1963) [Translated from Zh. Fiz. Khim. 37,
2761–2762 (1963)]. 2 fig., 1 tab., 9 ref.
A3 B1 C6 D1 E1 F7 G1 63
hydrogen, deuterium, liquid, viscosity, temperature effect

140. N. S. Rudenko and L. W. Schubnikov
Die Viskosität von Flüssigen stickstoff, Kohlenoxyd, Argon und Saurstoff in
Abhängigkeit von der Temperatur. (Viscosity of liquid nitrogen, carbon monoxide,
argon, and oxygen and its dependence on temperature.)
141. N. S. Rudenko and L. W. Schubnikov
Viskosität des flüssigen methans and athylens in abhangigkeit von der temperatur.
(Variation in the viscosity of liquid methane and ethylene with temperature.)
142. J. H. Rugheimer and P. S. Hubbard
Nuclear magnetic relaxation and diffusion in liquid CH$_4$, CF$_4$ and mixtures of CH$_4$ and CF$_4$ with argon.
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Simultaneous measurements of surface tension and viscosity of liquid argon by microbalance.
Cryogenics 4, 136–140 (1964). 8 fig., 1 tab., 10 ref.
144. Y. Saji and T. Okuda
Density, surface tension and viscosity measurements for the oxygen-argon system.
11 fig., 3 tab., 9 ref.
145. Y. Saji and T. Okuda
A certain excess property of the liquid system oxygen-argon.
19 fig., 11 tab., 17 ref.
146. C. Sakiadis and J. Coates
A literature survey of the thermal conductivity of liquids.
1952.
147. C. A. Schaefer
Thermal conductivity of diatomic fluids in the liquid and gaseous states.
6 tab., 211 ref.
halogen, bromine, chlorine, iodine, inorganic fluid, hydrogen bromide, hydrogen chloride, hydrogen fluoride, oxide of nitrogen, gaseous, liquid, thermal conductivity, reduced variable, law of corresponding states, carbon monoxide, fluorine, hydrogen, nitrogen, oxygen, compilation

148. C. A. Schaefer and G. Thodos
Reduced thermal conductivity correlation. Gaseous and liquid hydrogen.

149. C. A. Schaefer and G. Thodos
Thermal conductivity of diatomic gases: Liquid and gaseous states.

150. R. B. Scott

151. H. Shimotake
Viscosity-reduced state correlation for the inert gases.

152. R. Siev and S. K. Yoder
Hydrogen mass flow meter development.

153. R. B. Stewart and H. M. Roder
Properties of normal and parahydrogen.
"Technology and Uses of Liquid Hydrogen" (R. B. Scott, W. H. Denton, and
TRANSPORT PHENOMENA IN SIMPLE LIQUIDS

A3 B1 C6 D1 E2 F6 G2 64
hydrogen, parahydrogen, gaseous, PVT data, liquid, entropy, T-S diagram, heat of vaporization, heat of sublimation, specific heat, thermal conductivity, velocity of sound, viscosity, surface tension;
A3 B1 C6 D1 E2
hydrogen, parahydrogen, triple point, boiling point, critical constant, liquid, saturated liquid, density, solidified gas, gaseous, saturated vapor, vapor pressure, melting line

154. L. I. Stiel and G. Thodos
Viscosity of hydrogen in the gaseous and liquid states for temperatures up to 5000°K.
A3 B1 C6 D3 E2 F6 G1 63
hydrogen, gaseous, viscosity, density, reduced variable, saturated liquid, liquid, saturated vapor;
A6 B1 C6 D3 E2
fluid flow, liquid, gas, steady state, laminar, coefficient, viscosity, hydrogen

155. L. I. Stiel and G. Thodos
The thermal conductivity of nonpolar substances in the dense gaseous and liquid regions.
A3 B1 C1 D1 E2 F6 G1 64
thermal conductivity, liquid, gaseous, argon, krypton, xenon, nitrogen, oxygen, carbon monoxide, methane, compressibility factor, hydrocarbon, carbon dioxide

156. G. W. Swift, J. A. Christy, and F. Kurata
Liquid viscosities of methane and propane.
A3 B1 C7 D1 E1 F6 G1
viscosity, liquid, methane, propane, boiling-to-critical point

157. G. W. Swift, J. Lorenz, and F. Kurata
Liquid viscosities above the normal boiling point for methane, ethane, propane, and n-butane
A3 B1 C1 D1 E1 F6 G1
liquid, viscosity, methane, ethane, propane, butane, pressure dependence, temperature dependence

158. Thermophysical Properties Research Center.
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A3 B1 C8 D1 E2 F8 G2
gaseous, liquid, thermal conductivity, acetylene, Freon 22, refrigerant, freon 11, freon 12, freon 13, freon 21, freon 113, freon 114, viscosity, methyl chloride, organic fluid, acetone, benzene, ethane, halogen, bromine, iodine, chloroform, ethanol, methanol, butane, ethylene, hydrocarbon, paraffin glass, heptane, pentane, propane, ether, inorganic fluid, boron trifluoride, hydrogen chloride, halide, hydrogen, hydrogen sulfide, sulfur dioxide, argon, fluorine, methane, nitrogen, neon, oxygen, krypton, xenon, deuterium, oxide of nitrogen, water, halogen, chlorine, carbon tetrachloride, ethylene glycol, glycerol, toluene
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A3 B1 C3 D1 E2 F6 G1
viscosity, diffusion, liquid, rare gas

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A3 B1 C7 D1 E1 F6 G1
oxygen, liquid, gaseous, thermal conductivity, temperature effect

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specific heat, coefficient of expansion, compressibility, argon, carbon monoxide, 
methane, nitrogen, oxygen, hydrocarbon, velocity of sound, thermal conductivity, 
liquid, transport property

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argon, liquid, gaseous, thermal conductivity, nitrogen, pressure effect, high pressure, 
equation, Enskog formula, boiling point to critical point

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deuterium, liquid, viscosity, temperature effect

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hydrogen, deuterium, viscosity, liquid, hydrogen, argon, apparatus, nitrogen, 
carbon monoxide, oxygen, ethane

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viscosity, liquid, carbon monoxide, neon, argon, nitrogen, oxygen, hydrogen, 
methane, ethane, ammonia, chlorine, heat of vaporization

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viscosity, liquid, oxygen, nitrogen, argon, hydrogen, temperature effect
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neon, helium, argon, deuterium, hydrogen, ethane, carbon monoxide, oxygen, nitrogen, liquid, gaseous, viscosity

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viscosity, liquid, density, theory, high pressure, alcohol, methane, carbon tetrachloride, paraffin class, hydrocarbon, propane, pentane, mercury

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argon, nitrogen, gaseous, liquid, viscosity, temperature effect

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A3 B1 C6 D1 E1 F7 G1
hydrogen, liquid, viscosity

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thermal conductivity, ozone, oxygen, liquid

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A3 B1 C6 D1 E1 F9 G7
hydrogen, ortho-para hydrogen, viscosity, concentration effect, triple point, density, liquid, normal hydrogen, parahydrogen

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A3 B1 C6 D3 E1 F6 G1
hydrogen, parahydrogen, liquid, liquid mixture, viscosity

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helium, liquid, thermal conductivity, helium-4, solidified gas, gaseous, helium-3, argon, viscosity

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nitrogen, liquid, viscosity, density

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argon, viscosity, liquid, gaseous, density, temperature effect, isochore

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thermal conductivity, nitrogen, oxygen, argon, liquid, gaseous, critical region, temperature effect

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thermal conductivity, oxygen, liquid, 80° to 200°K, 1 to 300 atm

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nitrogen, argon, liquid, gaseous, thermal conductivity, oxygen, critical region

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