Transport Properties of a Dense Fluid of Molecules Interacting with a Square-Well Potential: Part II

K. D. LUKS, M. A. MILLER, and H. TED DAVIS

University of Minnesota, Minneapolis, Minnesota

The equations developed by Davis, Rice, and Sengers for the transport properties of a model fluid whose molecules interact according to a square-well potential are utilized herein to calculate the transport coefficients of krypton, xenon, and argon. With the use of theoretically determined pair correlation functions and experimental P-V-T data, results are obtained that indicate that the square-well theory provides a useful model for simple liquids. Master graphs of the transport coefficients as functions of reduced parameters are presented. An investigation of the relative importance of the contributions by kinetic transfer and by intermolecular collisional transfer leads to the conclusion that kinetic transfer can provide a sizable contribution to transport properties.

Recently Davis, Rice, and Sengers (*1*) presented a kinetic theory of transport for a model liquid whose molecules interact according to a square-well potential energy function. Their theory results in explicit formulas for the transport coefficients which depend on the parameters of the square-well potential and on the equilibrium pair correlation function of the liquid. Using an approximate pair correlation function, Davis and Luks (*2*) showed that the square-well formulas accounted for the viscosity and thermal conductivity of liquid argon over the entire liquid range. The approximate pair correlation function was obtained by multiplying a Boltzmann factor, accounting for the attractive portion of the square-well potential, by the expression for the pair correlation function for hard spheres. They used the hard sphere pair correlation function obtained by Wertheim (*3*) and Thiele (*4*) by solving the Percus-Yevick integral equation.

With the use of the approximate pair correlation function the formulas for the transport coefficients can be expressed in terms of the reduced parameters $x = \epsilon/kT$, $y = \pi\sigma_1^3\rho/6$, and $R = \sigma_2/\sigma_1$, where ϵ is the attractive depth of the square-well potential energy, σ_1 the hard sphere diameter, σ_2 the diameter measuring the range of the square-well attraction, k Boltzmann's constant, T the absolute temperature, and ρ the number density. In a subsequent section we will present master graphs for the transport coefficients as functions of the reduced parameters. These graphs represent a law of corresponding states for the transport coefficients and may prove useful for estimating transport properties of simple liquids.

Extension of the calculations to krypton and xenon is discussed later on. Again we find a good qualitative prediction of the thermal conductivity over the entire liquid range for these substances. In fact, for argon, krypton, and our particular choice of xenon parameters, predictions are accurate to ± 15%. Although the model works less well for diffusion than for the other transport properties, the predicted diffusivity of krypton is qualitatively correct and even quantitatively is never off by more than 35%.

We have examined the relative contributions of transport by kinetic transfer and that by intermolecular collisional transfer. This investigation is especially interesting, since several (*5* to *7*) recent theories of transport include only the intermolecular collisional contribution to transport. We find that, at least for the square-well model, the terms neglected by these theories cause up to 30% error, depending upon the temperature and density of the system in question.

THE TRANSPORT COEFFICIENTS FOR A SQUARE-WELL FLUID

A square-well fluid is defined as one composed of N particles which interact according to the pair potential

$$\begin{aligned} V(R_{ij}) &= 0, & R_{ij} &> \sigma_2 \\ V(R_{ij}) &= -\epsilon, & \sigma_1 &< R_{ij} \leqq \sigma_2 \qquad (1) \\ V(R_{ij}) &= +\infty, & R_{ij} &\leqq \sigma_1 \end{aligned}$$

where R_{ij} is the distance of separation of particles i and j. By definition, the force between square-well molecules is impulsive, that is, any collision occurs instantaneously. In fact this is the simplifying feature of the square-well interaction. In real liquids or dense fluids, a molecule is in continuous interaction with many molecules in the surrounding medium. Consequently, the concept of transport by binary collision, which has proved so useful in the analysis of transport properties of dilute gases, is not obviously relevant to the theory of transport in dense fluids. However, since collisions occur instantaneously in a square-well fluid, one may anticipate that energy and momentum exchange in these fluids, even at high densities, proceeds via binary collisions. In support of this thesis, one argues that in order for a molecule to experience a ternary collision, two other molecules must be at exactly the right points in space (either at $R_{ij} = \sigma_1$ or σ_2) at exactly the same instant. The likelihood of this occurrence is very small compared to that of a binary event which requires only that a second molecule move within a distance σ_1 or σ_2 of the first molecule. The possibility of a higher order collision than ternary would presumably be even more remote on the basis of the preceding argument.

Using the argument that only binary collisions are important in a square-well fluid, Davis, Rice, and Sengers (*1*) derived for this fluid a modified Maxwell-Boltzmann integro differential equation in which only binary collisions (occurring at $R_{ij} = \sigma_1$ or $R_{ij} = \sigma_2$) contributed to the dissipative process. The integro differential equation, when solved, eventually leads to the following formulas for the equation of state and the transport coefficients

Pressure:

$$P = \rho kT \{1 + b\rho [g(\sigma_1) + R^3 g(\sigma_2)(1 - e^{\epsilon/kT})]\} \tag{2}$$

Shear viscosity:

$$\eta = \eta^* \left\{ \frac{\left[1 + \frac{2}{5} b\rho (g(\sigma_1) + R^3 g(\sigma_2)\,\psi)\right]^2}{g(\sigma_1) + R^2 g(\sigma_2)\left[\boxed{H} + \frac{1}{6}(\epsilon/kT)^2\right]} + \frac{48}{25\pi}(b\rho)^2 (g(\sigma_1) + R^4 g(\sigma_2)\,\boxed{H}) \right\} \tag{3}$$

with

$$\eta^* = \frac{5}{16\sigma_1^2}\left(\frac{mkT}{\pi}\right)^{1/2} \tag{4}$$

Bulk viscosity:

$$\Phi = \eta^* \left\{ \frac{16}{5\pi}(b\rho)^2 [g(\sigma_1) + R^4 g(\sigma_2)\,\boxed{H}] \right\} \tag{5}$$

Diffusivity:

$$D = \frac{3}{8\rho\sigma_1^2}\left(\frac{kT}{\pi m}\right)^{1/2} [g(\sigma_1) + R^2 g(\sigma_2)\,\boxed{H}]^{-1} \tag{6}$$

This equation is the result of Longuet-Higgins and Valleau (*8*), who assumed that the momentum autocorrelation function decays exponentially with time.

Thermal conductivity:

$$\kappa = \kappa^* \left\{ \frac{\left[1 + \frac{3}{5} b\rho (g(\sigma_1) + R^3 g(\sigma_2)\,\psi)\right]^2}{g(\sigma_1) + R^2 g(\sigma_2)\left[\boxed{H} + \frac{11}{16}(\epsilon/kT)^2\right]} + \frac{32}{25\pi}(b\rho)^2 (g(\sigma_1) + R^4 g(\sigma_2)\,\boxed{H}) \right\} \tag{7}$$

with

$$\kappa^* = \frac{75}{64\sigma_1^2}\left(\frac{k^3 T}{\pi m}\right)^{1/2} \tag{8}$$

The functions $\boxed{H}$ and ψ are defined as

$$\boxed{H} = e^{\epsilon/kT} - \frac{\epsilon}{2kT} - 2\int_o^\infty x^2 (x^2 + \epsilon/kT)^{1/2} e^{-x^2}\, dx \tag{9}$$

$$\psi = 1 - e^{\epsilon/kT} + \frac{\epsilon}{2kT} \left[1 + \frac{4}{\sqrt{\pi}} e^{\epsilon/kT} \int_{\sqrt{\frac{\epsilon}{kT}}}^\infty e^{-x^2} x^2\, dx\right] \tag{10}$$

Also

$$b = 2\pi\sigma_1^3/3 \tag{11}$$

In Table 1, values are given for $\boxed{H}$ and ψ as a function of the arguments ϵ/kT and $(\epsilon/kT)^{1/2}$, respectively. The procedure for deriving Equations (2) through (8) is outlined in Davis and Luks (*2*) and the details of their calculation is given in Davis, Rice, and Sengers (*1*).

TABLE 1. VALUES OF $\boxed{H}$ AND ψ AS A FUNCTION OF THE ARGUMENTS ϵ/kT AND $(\epsilon/kT)^{1/2}$

ϵ/kT	$\boxed{H}$	$(\epsilon/kT)^{1/2}$	ψ
0	0.000000	0	0.000000
0.10	0.008650	0.08	−0.000001
0.20	0.032386	0.16	−0.000038
0.30	0.070994	0.24	−0.000290
0.40	0.125149	0.32	−0.001221
0.50	0.195904	0.40	−0.003740
0.60	0.284573	0.48	−0.009383
0.70	0.392705	0.56	−0.020549
0.80	0.522073	0.64	−0.040796
0.90	0.674682	0.72	−0.075242
1.00	0.852779	0.80	−0.131104
1.10	1.058876	0.88	−0.218439
1.20	1.295767	0.96	−0.351167
1.30	1.566558	1.04	−0.548500
1.40	1.874694	1.12	−0.836958
1.50	2.223995	1.20	−1.253229
1.60	2.618690	1.28	−1.848270
1.70	3.063464	1.36	−2.693227
1.80	3.563500	1.44	−3.888053
1.90	4.124532	1.52	−5.574180
2.00	4.752905	1.60	−7.953277
2.10	5.455632	1.68	−11.315297
2.20	6.240471	1.76	−16.080761
2.30	7.116000	1.84	−22.865104
2.40	8.091701	1.92	−32.577475
2.50	9.178057	2.00	−46.573845

DETERMINATION OF THE PAIR CORRELATION FUNCTION

In order to calculate the transport coefficients expressed by the above equations, one must determine the values of the parameters σ_1, σ_2, and ϵ and the pair correlation functions $g(\sigma_1)$ and $g(\sigma_2)$. Values of the parameters have been determined empirically from gaseous data for several compounds (9). With respect to obtaining values of the pair correlation functions, one approach that can be taken is the semiempirical procedure of solving the square-well equation of state and one of the square-well transport coefficient equations simultaneously by using available PVT data and, for example, liquid viscosity data. This procedure yields values of $g(\sigma_1)$ and $g(\sigma_2)$ which can be used to calculate the thermal conductivity of the liquid at the same PVT conditions. It is more useful, however, to use theoretically determined values of the pair correlation function.

Lowry, Davis, and Rice (*10*) have developed a perturbation technique for calculating the equilibrium pair correlation function. The theory assumes that the pair potential energy can be separated into two contributions:

$$V(R_{12}) = V^{(0)} + V^{(1)}$$

where

$V^{(0)}$ = unperturbed potential energy

and

$V^{(1)}$ = perturbation potential energy

$V^{(1)}$ is assumed to be less than kT. The pair correlation function is then found to be given by

$$g(R_{12}) = g^o(R_{12})\, e^{-\beta v^{(1)}(R_{12})} [1 + \theta(R_{12})] \tag{12}$$

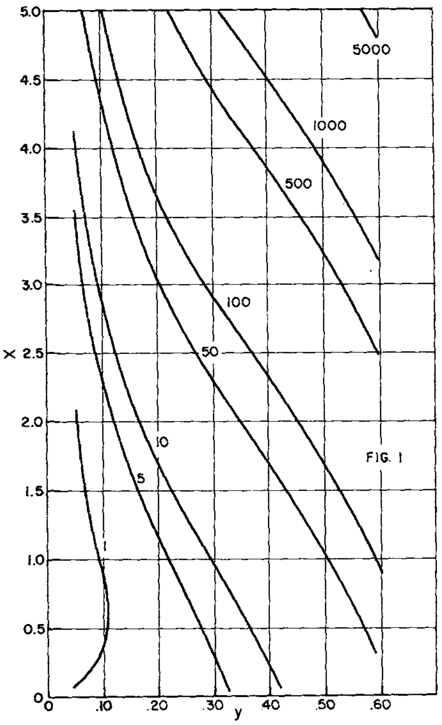

Fig. 1. Reduced inverse temperature x vs. reduced density y for several values of reduced viscosity η/η^*; $R = 1.50$.

in which $g^o(R_{12})$ is the pair correlation function for particles interacting according to the unperturbed potential energy, $e^{-\beta V^{(1)}(R_{12})}$ is the Boltzmann factor arising from the perturbation pair interaction between particles 1 and 2, and $\theta(R_{12})$ is an effect due to the presence of many interacting particles in the vicinity of particles 1 and 2. In calculating transport coefficients, the lowest approximation for $g(R_{12})$ shall be used, that is, $\theta(R_{12})$ shall be neglected. This is admittedly a weak point in our analysis; but on the basis of the results of Davis and Luks (*2*) for liquid argon, we feel at least a posteriori justification for neglecting $\theta(R_{12})$. Lowry, Rice, and Davis found that for a perturbation interaction strength of the order $\beta\epsilon \sim 0.5$ and at liquid argon densities, the contribution arising from $\theta(R_{12})$ can be neglected.

For the square-well model we choose the unperturbed part of the potential energy to be the hard-core part:

$$\begin{aligned} V^{(0)}(R_{12}) &= 0, & R_{12} &> \sigma_1 \\ &= +\infty, & R_{12} &\leqq \sigma_1 \end{aligned} \tag{13}$$

with the attractive well constituting the perturbation

$$\begin{aligned} V^{(1)}(R_{12}) &= 0, & R_{12} &> \sigma_2 \\ &= -\epsilon, & \sigma_1 < R_{12} &\leqq \sigma_2 \\ &= 0, & R_{12} &\leqq \sigma_1 \end{aligned} \tag{14}$$

In terms of Equations (3) and (14), the first approximation to Equation (12) is

$$g(R_{12}) \simeq g^o(R_{12})\, e^{-\beta V^{(1)}(R_{12})} \tag{15}$$

where $g^o(R_{12})$ is the pair correlation function for a fluid of rigid spheres.

Several approximate integral equations have been developed for the equilibrium pair correlation function (*11*). Of these, the integral equation of Percus and Yevick (*12*) appears to be quite satisfactory for the hard sphere fluid. The equation of state predicted on the basis of the Percus-Yevick equation not only yields good agreement with known values of virial coefficients, but also quantitatively reproduces the Monte Carlo results for the equation of state of hard spheres (*13*). Wertheim (*3*) and Thiele (*4*) have solved the Percus-Yevick equation exactly for the case of hard spheres, the result being an explicit equation for the pair correlation function. For the range $\sigma_1 < R_{12} < 2\sigma_1$, Wertheim obtained the formula

$$x g^o(x) = (1-y)^{-2} \sum_{l=0}^{2} A_l \exp[t_l (x-1)] \tag{16}$$

where

$$\begin{aligned} x &= R_{12}/\sigma_1 \\ y &= \pi \sigma_1^3 \rho/6 \\ A_l &= \frac{1}{3} \sum_{m=0}^{2} H_m j^{ml} \\ t_l &= 2y(1-y)^{-1}[-1 + \chi_+ j^l + \chi_- j^{-l}] \end{aligned} \tag{17}$$

with the further definitions

$$f = (3 + 3y - y^2)/4y^2$$

$$j = \exp\left(\frac{2}{3}\pi i\right)$$

$$\chi_\pm = \left[f \pm \left(f^2 + \frac{1}{8}\right)^{1/2}\right]^{1/3}$$

$$H_o = 1 + \frac{1}{2} y \tag{18}$$

$$H_1 = -(4y)^{-1}\left(f^2 + \frac{1}{8}\right)^{-1/2} \left[\chi_-^2 (1 - 3y - 4y^2) + \chi_+ \left(1 - \frac{5}{2} y^2\right)\right]$$

$$H_2 = (4y)^{-1}\left(f^2 + \frac{1}{8}\right)^{-1/2}$$

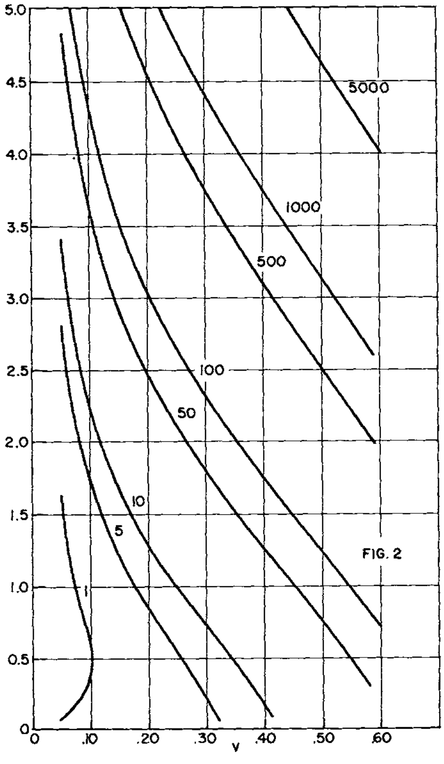

Fig. 2. Reduced inverse temperature x vs. reduced density y for several values of reduced viscosity η/η^*; $R = 1.90$.

$$\left[\chi_+^2(1-3y-4y^2)+\chi_-\left(1-\frac{5}{2}y^2\right)\right]$$

For the liquids considered in this paper, $R < 2$; consequently there is no need for the more complicated equations for $g^0(x)$ for $x > 2$. Throop and Bearman (*14*) have done a complete numerical analysis of the Wertheim solution.

MASTER GRAPHS OF VISCOSITY, THERMAL CONDUCTIVITY, AND DIFFUSIVITY

Since we are using an approximate pair correlation function we shall not consider further the theoretical equation of state, Equation (2), because it is much more sensitive to errors in the correlation function than are the transport coefficients. The reason for this is that the pressure is a small quantity arising from the difference between a large attractive force effect and a large repulsive force and thermal effect. Thus any approximation made on the pair correlation function gives a magnified error in pressure. On the other hand, in the formulas for the transport coefficients the repulsive and attractive effects have the same sign. Thus the transport coefficients are not as sensitive as pressure to the use of approximate pair correlation functions.

With Equations (2) through (8) master graphs can be constructed from which the behavior of the transport coefficients as a function of (x, y, R) can be studied. Figures 1 and 2 are plots of lines of constant η/η^* as a function of x and y, each graph being for a particular R. Figures 3 through 6 are parallel plots for κ/κ^* and D/D^* where

$$D^* = \frac{3}{8\rho\sigma_1^2}\left(\frac{kT}{\pi m}\right)^{1/2} \tag{19}$$

With a knowledge of the square-well parameters for a compound, the temperature and density dependence of θ, where $\theta = \eta, \kappa, D$, can be easily portrayed for $R = 1.50$ and 1.90. By means of interpolation, transport properties can be estimated with these plots.

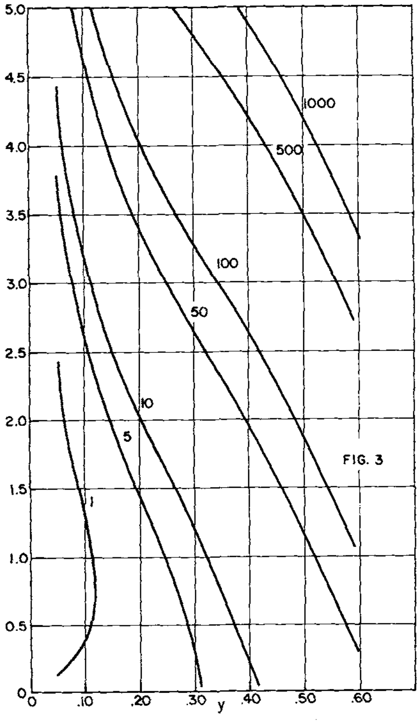

Fig. 3. Reduced inverse temperature x vs. reduced density y for several values of reduced thermal conductivity κ/κ^*; $R = 1.50$.

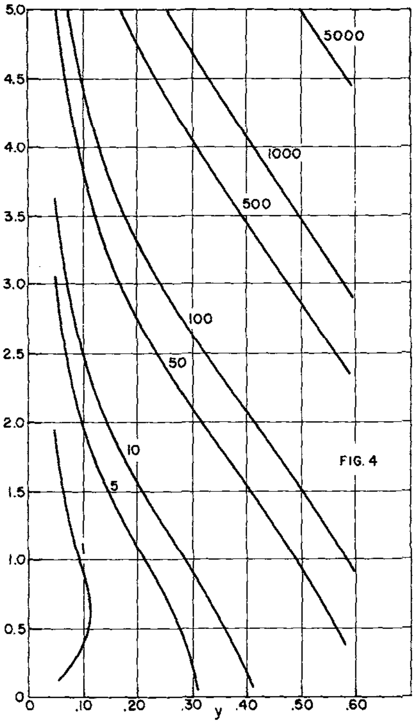

Fig. 4. Reduced inverse temperature x vs. reduced density y for several values of reduced thermal conductivity κ/κ^*; $R = 1.90$.

For the available square-well parameters of argon and krypton, the use of the master graphs have yielded predictions that differ from experimental data less than ± 15% for viscosity and thermal conductivity. The agreement is not as good for diffusivity. Comparisons are discussed in greater detail in the next section.

COMPARISON WITH EXPERIMENT FOR THE NOBLE LIQUIDS

In our previous article (*2*), calculations of the viscosity, thermal conductivity, and the diffusivity for liquid argon were performed and were compared with experimental data. In this section we shall discuss comparisons with experiment of the transport coefficients for liquid krypton and xenon.

The principal problem in making predictions is the selection of the square-well parameters σ_1, R, and ϵ/k for the model. Hirschfelder, Curtiss, and Bird (9) present square-well parameters determined from virial coefficient data for krypton, which prove satisfactory for use in the transport equations. However, no source was found for parameters for xenon. The choice of xenon parameters shall be discussed later.

For krypton:

$$\begin{aligned}\sigma_1 &= 3.362 \text{ Å.}\\ R &= 1.85\\ \epsilon/k &= 98.3 \text{ °K.}\end{aligned} \tag{20}$$

Density data at saturation for the noble liquids were obtained from Cook (*15*), while the generalized charts of Hougen, Watson, and Ragatz (*16*) were used in computing the remainder of the liquid density data.

Calculations of the thermal conductivity of liquid krypton were performed over the temperature range of 125° to 200°K. for pressures up to 500 atm. Agreement is good over the entire range, with the best agreement occurring at the lower temperatures (< ± 5%).

By using the equation of Lonquet-Higgins and Valleau (*8*), comparison for liquid krypton was made of the

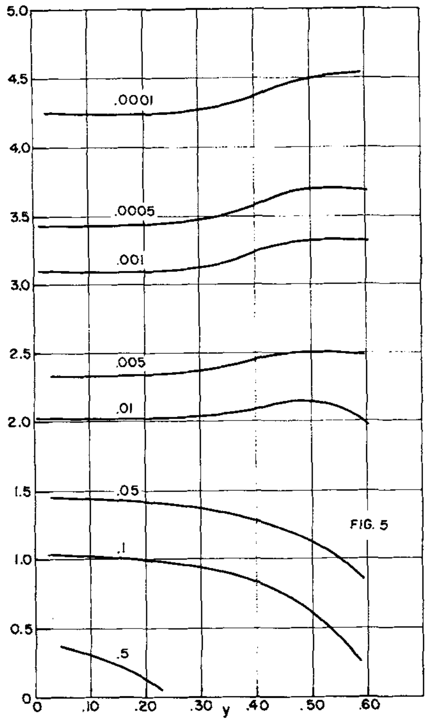

Fig. 5. Reduced inverse temperature x vs. reduced density y for several values of reduced diffusivity D/D^*; $R = 1.50$.

square-well diffusivity with the experimental data of Naghizadeh and Rice (*18*). The predictions were generally low by about 30% but, as was the case with liquid argon (2), the predicted temperature dependency—and hence the activation energy—was close to experiment.

An educated guess of the xenon parameters was attempted. While Hirschfelder, Curtiss, and Bird (9) listed square-well parameters for only argon and krypton, they listed Lennard-Jones parameters (determined by the same method as the square-well parameters, that is, from virial coefficient data) for xenon as well. Comparison of the square-well parameters with the Lennard-Jones parameters yielded the following interesting results:

$$\frac{\left[\left(\frac{\epsilon}{k}\right)_{Ar}\right]_{SW}}{\left[\left(\frac{\epsilon}{k}\right)_{Ar}\right]_{LJ}} \approx \frac{\left[\left(\frac{\epsilon}{k}\right)_{Kr}\right]_{SW}}{\left[\left(\frac{\epsilon}{k}\right)_{Kr}\right]_{LJ}} \qquad (21)$$

and

$$\frac{(\sigma_{1Ar})_{SW}}{(\sigma_{1Ar})_{LJ}} \approx \frac{(\sigma_{1Kr})_{SW}}{(\sigma_{1Kr})_{LJ}} \qquad (22)$$

By assuming constancy of R (that is, $R = 1.85$) and constancy of the ratios in Equations (21) and (22) for xenon as well, the following set of parameters for xenon was obtained: $R = 1.85$, $\sigma_1 = 3.819$ Å., and $\epsilon/k = 126.52$°K. Upon using these parameters to predict thermal conductivity and by comparing the results with the experimental data for xenon of Ikenberry and Rice (*17*), it was found that the predicted values were high by a factor of approximately 5/3. By noting that the square-well thermal conductivity is a more sensitive function of σ_1 than of ϵ/k, σ_1 was altered to agree with the experimental data at 170.24°K. The resulting value of σ_1 was 3.54 Å. Consequently, the choice of parameters for xenon was

$$\begin{aligned} \sigma_1 &= 3.54 \text{ Å.} \\ R &= 1.85 \\ \epsilon/k &= 126.52\text{°K.} \end{aligned} \qquad (23)$$

Calculations of the thermal conductivity of liquid xenon were performed and compared with experiment (*17*) for the temperature range of 170° to 235°K. for pressures up to 500 atm. Agreement was excellent over the entire liquid range, with the maximum deviations being < 10% at the high temperatures. Perhaps this agreement could be improved if one were to fit the parameters in a like manner to data in the middle of the liquid range, rather than at one end of the range. Also, the parameters could perhaps be improved by requiring the equation of state (*2*) *to fit the xenon* PVT data.

This choice of parameters for xenon, based on experimental data, is likely not a true description of the intermolecular potential of the liquid. For instance, the parameters will not correctly predict the second virial coefficient of gaseous xenon. However, this is immaterial, since we are concerned with liquid properties for which phase the parameters might be different from those predicted from gaseous data. The support for our choice of parameters is the consistent accuracy of the predicted thermal conductivity throughout the wide liquid region tested. It should not be assumed however, that this set of parameters is the only set that will yield consistent predictions.

It should be noted that we have attempted to predict transport coefficients for more complex liquids, for example, water and hexane, using parameters from Hirschfelder, Curtiss, and Bird. The results, quantitatively speaking, were very poor, indicating that the internal degrees of freedom must be included in a theory of transport for polyatomic fluids.

RELATIVE CONTRIBUTIONS OF KINETIC AND COLLISIONAL TRANSPORT PROCESSES TO VISCOSITY AND THERMAL CONDUCTIVITY

The transport coefficient ratios η/η^* and κ/κ^* are composed of terms arising from kinetic and intermolecular transport processes. These ratios can be broken down into three parts, or contributions, with the following description:

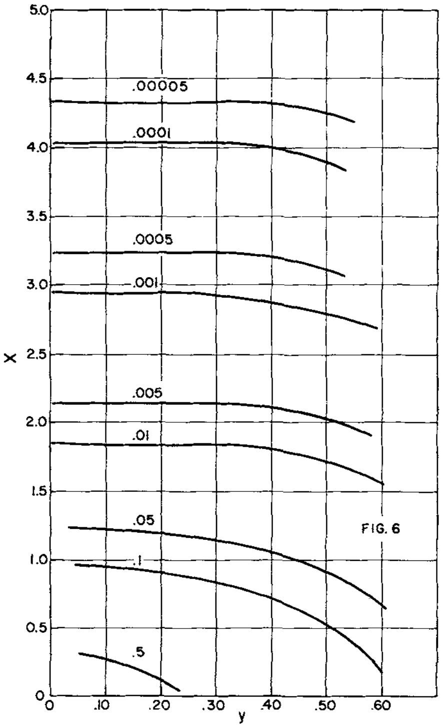

Fig. 6. Reduced inverse temperature x vs. reduced density y for several values of reduced diffusivity D/D^*; $R = 1.90$.

1. The kinetic contribution, θ_K/θ^*.
2. The intermolecular contribution, θ_V/θ^*.
3. The intermolecular contribution due to the perturbation to the singlet distribution function, θ_{KV}/θ^* where $\theta = \eta, \kappa$.

The kinetic contribution θ_K is the momentum or energy transferred across a surface due to the actual motion of the molecule across the surface. In this case the momentum or energy transferred is the momentum or kinetic energy of the molecule. The term θ_V represents the contribution due to a binary collisional transfer across a surface between two molecules which are at local equilibrium on their respective sides of the plane. θ_{KV} represents a binary collisional contribution due to the deviation of the two molecules from local equilibrium, that is, this term is due to the deviation of the singlet distribution function from the local Maxwellian distribution. Incidentally, θ_K is the only contribution in a dilute gas.

The general behavior of the equations for η/η^* and κ/κ^* shall be examined with respect to the above-mentioned contributions, which are

$$\eta_K/\eta^* = \frac{1 + \frac{2}{5} b\rho \left[g(\sigma_1) + R^3 g(\sigma_2)\, \psi\right]}{g(\sigma_1) + R^2 g(\sigma_2) \left[\boxed{H} + \frac{1}{6}\left(\frac{\epsilon}{kT}\right)^2\right]} \tag{24}$$

$$\eta_V/\eta^* = \frac{48}{25\pi} (b\rho)^2 \left[g(\sigma_1) + R^4 g(\sigma_2) \boxed{H}\right] \tag{25}$$

$$\eta_{KV}/\eta^* = (\eta - \eta_K - \eta_V)/\eta^* \tag{26}$$

$$\kappa_K/\kappa^* = \frac{1 + \frac{3}{5} b\rho \left[g(\sigma_1) + R^3 g(\sigma_2)\, \psi\right]}{g(\sigma_1) + R^2 g(\sigma_2) \left[\boxed{H} + \frac{11}{16}\left(\frac{\epsilon}{kT}\right)^2\right]} \tag{27}$$

$$\kappa_V/\kappa^* = \frac{32}{25\pi} (b\rho)^2 \left[g(\sigma_1) + R^4 g(\sigma_2) \boxed{H}\right] \tag{28}$$

$$\kappa_{KV}/\kappa^* = (\kappa - \kappa_K - \kappa_V)/\kappa^* \tag{29}$$

The relative contributions shall be calculated in this section as fractions, that is

$$\text{kinetic contribution to } \eta = \eta_K/\eta \tag{30}$$

$$\eta_K/\eta + \eta_V/\eta + \eta_{KV}/\eta = 1 \tag{31}$$

The behavior of the contributing fractions shall be determined as a function of the reduced density y, with the following values of the parameter R and the variable ϵ/kT:

$$\begin{aligned} R &= 1.90 \\ \epsilon/kT &= 0.10,\quad 0.80 \end{aligned} \tag{32}$$

TABLE 2. FRACTIONAL CONTRIBUTIONS TO SQUARE-WELL VISCOSITY AND THERMAL CONDUCTIVITY

$R = 1.90, x = 0.10$

y	η_K/η	η_V/η	η_{KV}/η	κ_K/κ	κ_V/κ	κ_{KV}/κ
0.10	0.709	0.128	0.161	0.688	0.076	0.235
0.20	0.392	0.370	0.237	0.409	0.219	0.371
0.30	0.199	0.554	0.247	0.231	0.338	0.430
0.40	0.100	0.662	0.236	0.128	0.419	0.452
0.50	0.050	0.724	0.224	0.069	0.470	0.459
0.60	0.025	0.758	0.216	0.035	0.501	0.463

TABLE 3. FRACTIONAL CONTRIBUTIONS TO SQUARE-WELL VISCOSITY AND THERMAL CONDUCTIVITY

$R = 1.90, x = 0.80$

y	η_K/η	η_V/η	η_{KV}/η	κ_K/κ	κ_V/κ	κ_{KV}/κ
0.10	0.192	0.768	0.039	0.231	0.697	0.070
0.20	0.064	0.889	0.046	0.089	0.813	0.097
0.30	0.033	0.906	0.060	0.051	0.809	0.138
0.40	0.019	0.906	0.073	0.032	0.789	0.178
0.50	0.011	0.903	0.084	0.019	0.769	0.211
0.60	0.006	0.889	0.103	0.011	0.728	0.259

The y dependence of the contributing fractions to η and κ are given in Tables 2 and 3. In regard to these tables, the increasing of the value of ϵ/kT for a given R reveals the effect of temperature decrease (or well depth increase) on the contributions.

The predictions in Table 2 are for a relatively high-temperature fluid ($\epsilon/kT = 0.1$). At this temperature the fractional contributions do not differ greatly from the corresponding fractional contributions calculated from the Enskog hard sphere formulas which may be obtained from Equations (2) to (7) by setting $\epsilon/kT = 0$. The hard sphere calculations are given in Table 4. It is interesting to note that at these high temperatures, the total viscosity and thermal conductivity predicted by the square-well model differ very little from hard sphere predictions. The predictions based on these models are compared in Table 5. Even at very high densities, for example, $y = 0.60$, the hard sphere and the square-well predictions agree to within 8%. (The density of a molten alkali halide around its melting point would correspond roughly to a reduced density of $y = 0.40$.) Michels, Sengers et al. (19) have found that the Enskog hard sphere formulas may be successfully applied to several dense gases (nitrogen, carbon dioxide, neon, and argon) even at room temperature where $x = 0.2$. Thus it seems that for dense gases at high temperature, that is, $0 \leqq \epsilon/kT \leqq 0.2$, the attractive part of the pair potential may be neglected in predicting the transport coefficients. It is interesting to note in Table 4 that even at very high densities, the sum of the contributions θ_K and θ_{KV} contributes 25% to the viscosity and 50% to the thermal conductivity. Thus a local equilibrium theory (that is, one involving the assumption that the singlet distribution function is of the local Maxwellian form) would not be adequate at all in the range $0 \leqq x \leqq 0.2$.

In a temperature range characteristic of liquids, which is roughly speaking $1 < x < 0.4$ for the noble liquids, the hard sphere formulas no longer give adequate predictions of the transport coefficients. In fact for liquid argon at 91.0°K. and at 1.5 atm. the viscosity and thermal conductivity predicted by the square-well theory are, respectively, 2.5 and 1.8 times the predictions of the hard sphere theory. In Table 3 we give the fractional contributions to η and κ for $x = 0.8$ and $R = 1.90$. Throughout

TABLE 4. FRACTIONAL CONTRIBUTIONS TO HARD SPHERE VISCOSITY AND THERMAL CONDUCTIVITY

y	η_K/η	η_V/η	η_{KV}/η	κ_K/κ	κ_V/κ	κ_{KV}/κ
0.10	0.744	0.101	0.154	0.717	0.059	0.223
0.20	0.435	0.324	0.239	0.445	0.187	0.367
0.30	0.227	0.517	0.255	0.257	0.308	0.434
0.40	0.115	0.639	0.245	0.143	0.396	0.459
0.50	0.058	0.709	0.232	0.078	0.454	0.468
0.60	0.028	0.750	0.221	0.040	0.489	0.469

TABLE 5. COMPARISON OF η/η^* AND κ/κ^* FOR THE SQUARE-WELL AND HARD SPHERE MODELS

($R = 190$, $x = 0.10$)
(SW = square-well; HS = hard sphere)

y	$(\eta/\eta^*)_{SW}$	$(\eta/\eta^*)_{HS}$	$(\kappa/\kappa^*)_{SW}$	$(\kappa/K^*)_{HS}$
0.10	1.177	1.251	1.311	1.411
0.20	2.116	2.070	2.387	2.390
0.30	4.286	3.992	4.679	4.472
0.40	8.960	8.160	9.444	8.799
0.50	19.099	17.223	19.606	18.020
0.60	42.400	38.133	42.821	39.084

the density range considered in these tables, the contributions of θ_K and θ_{KV} are appreciable for both η and κ. For all densities in Table 3, the sum of θ_K and θ_{KV} contributes about 10% of the total viscosity and 20 to 25% of the total thermal conductivity.

It is possible that the relative importance of θ_K and θ_{KV} in liquids arises from the singular nature of square-well and hard sphere forces. To examine this possibility it is useful to compare the fractional contributions based on the square-well model to the corresponding quantities predicted by the Rice-Allnatt (*20, 21*) theory of transport, which does not depend on restrictive assumptions concerning the nature of the interaction potential. Rice and Grey (*22*) have performed calculations of the various contributions to viscosity and thermal conductivity for liquid argon by using the equations resulting from the Rice-Allnatt theory. Their calculations were based on a Lennard-Jones potential model. They took the appropriate pair correlation functions from the superposition theory calculations of Kirkwood, Lewinson, and Alder (*23*), whose method involves an expansion in powers of ϵ/kT where ϵ is the depth of the Lennard-Jones potential describing the interaction between the molecules. Table 6 compares the fractional contributions to the transport coefficients for the square-well theory and the Rice-Allnatt theory. The relative contribution of the intermolecular part of η and κ is much larger for the Rice-Allnatt theory than for the square-well theory. This indicates that perhaps the neglect of $\theta_K + \theta_{KV}$ is not as serious an approximation for a real liquid as one might estimate on the basis of a square-well or hard sphere model. On the other hand, there is some uncertainty in the calculations of Rice and Grey because of the approximate nature of the pair correlation function they used, so that the effect of $\theta_K + \theta_{KV}$ could be somewhat larger, or smaller for that matter. In any case we feel that any theory attempting to predict the transport coefficients of liquids to better than 85% accuracy should include the contributions θ_K and θ_{KV}. This is unfortunate, because generally speaking θ_V is easier to obtain theoretically than θ_K and θ_{KV}.

TABLE 6. COMPARISON OF SQUARE-WELL FRACTIONAL CONTRIBUTIONS WITH RICE-ALLNATT CONTRIBUTIONS FOR LIQUID ARGON

(SW = square-well; RA = Rice-Allnatt)

T, °K.	P, atm.	η_K/η (SW)	η_K/η (RA)	η_V/η (SW)	η_V/η (RA)	η_{KV}/η (SW)	η_{KV}/η (RA)
90	1.3	0.032	0.022	0.884	0.969	0.082	0.009
128	50	0.089	0.086	0.781	0.830	0.128	0.084
133.5	100	0.092	0.087	0.771	0.860	0.135	0.053

T, °K.	P, atm.	κ_K/κ (SW)	κ_K/κ (RA)	κ_V/κ (SW)	κ_V/κ (RA)	κ_{KV}/κ (SW)	κ_{KV}/κ (RA)
90	1.3	0.050	0.019	0.757	0.965	0.192	0.016
128	50	0.123	0.039	0.610	0.919	0.265	0.042
133.5	100	0.127	0.054	0.594	0.903	0.278	0.043

REMARKS

We feel that the success of the square-well model in predicting transport coefficients for the noble liquids substantiates its validity as an approximate description of a simple liquid. It should be reemphasized that the strength of the square-well model lies in its relative simplicity and its ability to be used with quantities that can be wholly determined by theoretical means, once the potential parameters are known. The results of our calculations lead us to believe that in liquids as loosely packed as the noble liquids the kinetic contributions must be retained.

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NOTATION

$b \quad = \dfrac{2}{3}\pi\sigma_1^3$
$D \quad$ = diffusivity
$D^* \quad = \dfrac{3}{8\rho\sigma_1^2}\left(\dfrac{kT}{\pi m}\right)^{1/2}$
$g(\sigma_1)$ = value of the pair correlation function at σ_1
$g(\sigma_2)$ = value of the pair correlation function at σ_2
$g^o(R_{12})$ = hard sphere pair correlation function
$\boxed{H} \quad = e^{\epsilon/kT} - \dfrac{\epsilon}{2kT} - 2\int_0^\infty x^2(x^2 + \epsilon/kT)^{1/2}\, e - x^2\, dx$
k = Boltzmann's constant
LJ = Lennard-Jones
m = mass of particle
P = pressure
R = σ_2/σ_1
SW = square-well
T = temperature
$V^{(0)}$ = unperturbed potential energy
$V^{(1)}$ = perturbation potential energy
$V(R_{ij})$ = intermolecular potential where R_{ij} = distance between particles i and j
x = R_{12}/σ_1
$y \quad = \dfrac{1}{6}\pi\sigma_1^3\rho$

Greek Letters

β = $1/kT$
ϵ = depth of square-well potential
θ = transport coefficient
θ_k = kinetic contribution to transport coefficient
θ_v = intermolecular contribution to transport coefficient
θ_{kv} = perturbation contribution to transport coefficient
η = shear viscosity
$\eta^* \quad = \dfrac{5}{16\sigma_1^2}\left(\dfrac{mkT}{\pi}\right)^{1/2}$
κ = thermal conductivity
$\kappa^* \quad = \dfrac{75}{64\sigma_1^2}\left(\dfrac{k^3T}{\pi m}\right)^{1/2}$
ρ = number density
σ_1 = inner boundary of square-well potential
σ_2 = outer boundary of square-well potential
Φ = bulk viscosity

$$\psi = 1 - e^{\epsilon/kT} + \frac{\epsilon}{2kT} \left[1 + \frac{4}{\pi} e^{\epsilon/kT} \int_{\sqrt{\epsilon/kT}}^{\infty} e^{-x^2} x^2 \, dx \right]$$

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Flow in Concentric Annuli at High Reynolds Numbers

R. R. ROTHFUS, W. K. SARTORY, and R. I. KERMODE

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

A method is proposed and developed for predicting velocity profiles in smooth, concentric annuli at high Reynolds numbers from the profiles in equivalent tubes. Experimental data for the flow of water in two annuli with diameter ratios of 14.8 and 38.2 at Reynolds numbers up to 226,000 strongly support the predictions. Published data show the method to be successful over a very wide range of diameter ratios.

The problem of flow in noncircular ducts is an old and difficult one. When the motion is turbulent, it is customary to compare the fluid behavior with that in an equivalent tube. The practical problem is to find the proper conditions for comparison.

Concentric annuli are especially interesting noncircular ducts for they have two continuous, easily described boundaries, each exerting uniform but different skin frictions on the fluid. As the diameter ratio passes to its limits, the configuration goes to a tube on one hand and parallel plates on the other. When an annulus is compared with a tube, it is therefore being compared with another type of annulus rather than an entirely different kind of duct.

Barring unexpected complications, the rules governing flow in a tube have a good chance of applying generally to the portion of an annulus between the radius of maximum fluid velocity and the outer wall. If the rules apply equally well to both the inner and outer parts of the annular duct, both sides of the maximum point can be related to respective equivalent tubes through the same kind of generality.

When the annular flow is entirely laminar, the radius of maximum velocity is such that the comparison with tubular flow can be made by means of straightforward

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W. K. Sartory is with Oak Ridge National Laboratory, Oak Ridge, Tennessee.