Predictive Equations for Self-Diffusion in Liquids: a Different Approach

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Simple relationships have been obtained which can be used to predict self-diffusion coefficients of liquids with an average error of ±4%. In addition to the customary parameters, one of these equations contains the critical volume

$$\frac{\mu VD}{RT} = 0.124 \times 10^{-16} V_c^{2/3}$$

whereas the other uses Lennard-Jones potential parameters

$$\frac{\mu VD}{RT} = 0.129 \times 10^{-16} \sigma^2 (\Omega_D \Omega_V)^{1/2} T_c$$

Both relations were derived by using a general relation between transport coefficients of pure fluids and a molecular-kinetic-model of liquids. No use has been made either of the Stokes-Einstein relation or the absolute rate theory.

By applying the same relation between transport coefficients of pure fluids to gases, an equation has been obtained which can be used to calculate consistently molecular diameters in gases as a function of temperature, using Lennard-Jones potential parameters.

A number of relationships have been proposed in the literature between diffusion coefficients and viscosity of liquids. The oldest of these is probably the Stokes-Einstein Equation (*1*), and one of the most sophisticated ones is the Wilke-Chang correlation (*2*). For the special case of self-diffusion, Li and Chang (*3*) gave the following relationship, assuming that the molecules in the liquid are arranged in a cubic lattice with all molecules just touching:

$$\frac{D\mu}{kT} = \frac{1}{2\pi}\left(\frac{N}{V}\right)^{1/3} \tag{1}$$

This relationship was obtained by a modification of the Stokes-Einstein equation and also by a modification of Eyring's theory. In the latter case a factor of 6 was obtained instead of 2π, for the case of simple cubic packing. Subsequently, McLaughlin (*43*) tested Equation (1) with eight systems and found empirically 2.035π for the average value of the numerical coefficient in Equation (1), with a mean deviation of ± 10%.

In the present paper a relationship which is constructed somewhat similarly as Equation (1) has been derived without making any use of either the Stokes-Einstein relation or the absolute rate theory.

The new equation is based on a simple molecular model of the liquid, and it is capable of predicting self-diffusion coefficients with a mean deviation of ± 4%. The equation does not contain any adjustable parameters.

The starting point of the analysis is a relationship between the viscosity and the two tracer diffusion coefficients in binary solutions (*4*), which was later generalized by Snell and Spangler (*5*) to multicomponent systems. For binary systems, the relation is

$$\delta = \sqrt{\frac{2\mu V}{RT(N_A/D_{AA} + N_B/D_{BB})}} \tag{2}$$

whereas for one component systems it simplifies to

$$\delta = \sqrt{\frac{2\mu VD}{RT}} \tag{3}$$

Equations (2) and (3) were not based on any particular molecular model of the substance and can be expected to apply to Newtonian fluids, in general. These are the only relationships of this kind which can be expected to be valid for gases as well as liquids. It has been shown by the author (*4*) that if the elementary kinetic gas theory expressions for the self-diffusion coefficient, the viscosity, and the mean free path are introduced into Equation (3), one obtains $\delta = 2/3\lambda$, which is a well-known result from the elementary kinetic theory.

In the theoretical part of this paper, molecular interpretation has been given to δ for liquids, and, as a result, a relationship has been obtained between molecular diameters in liquids and the right-hand side of Equation (3). The values obtained for molecular diameters are plausible values without exception.

From the engineering point of view, the prediction of self-diffusion coefficients of liquids from other measurable quantities is of some interest. One approach might consist of a group contribution method for the prediction of proper molecular diameters to estimate self-diffusion coefficients of liquids. Before such a laborious task is tackled, however, it would be desirable to have a greater number of accurate self-diffusion data than presently available. In the present paper a different and far simpler correlation is proposed in which the molecular diameter is calculated from the critical volume.

THEORY

Relationship Between δ and Molecular Diameter

The model to be used for liquids at temperatures not very far from the melting point consists of disordered as-

semblages of interacting bodies. Owing to the presence of attractive forces, the bodies tend to stay in contact with their immediate neighbors most of the time. Therefore, translational motion is practically impossible, and each molecule keeps oscillating between its immediate neighbors, exchanging momentum every time collision takes place, as it was proposed by Andrade (*6, 16*). According to this model of a liquid, mass transport is due to small displacements of the molecular centers in the course of every oscillation. At higher temperatures, as the number density decreases, it is assumed that the molecules do not get distributed completely randomly over the space available for them, but, owing to the presence of attractive forces, they maintain a coherent structure with voids of varying sizes distributed in the irregular lattice formed by the molecules (*7, 8, 14*). Under such conditions a fraction of the molecules can be assumed to be in translational motion in the void spaces; that is, at higher temperatures part of the momentum transfer takes place by a similar mechanism as in gases.

In a first approximation it is assumed that the molecules are rigid; that is, the molecular diameters do not vary with the temperature. This restriction, however, can be easily lifted by introducing a temperature dependence according to some potential function.

In order to derive a relationship between δ and the molecular diameter based on the above model of the liquid near its melting point, it is useful to clarify the physical meaning of δ in terms of Newton's law of viscosity

$$\tau_{zy} = -\mu \frac{dv_y(z)}{dz} \tag{4}$$

where τ_{zy} is the y momentum transferred in the z direction per unit area per unit time by molecules of the fluid at $z - \delta$ to molecules at z.

Before the derivation is made, two more assumptions are made. It is assumed that when the present model of a liquid is intersected with a plane parallel to the direction of shear (parallel to the xy plane) the plane intersects a molecule with equal probability at any distance from its centre, and the orientation of a pair consisting of two touching molecules is random, which means that there is equal probability for such a pair to be oriented in any range of solid angles $d\omega = \sin\theta\, d\theta\, d\phi$. One such pair of molecules intersected by a plane is shown in Figure 1. It is apparent from the figure that part of each of the two molecules is on one side of the plane (marked by $'$), while the other part is on the other side (marked by $''$).

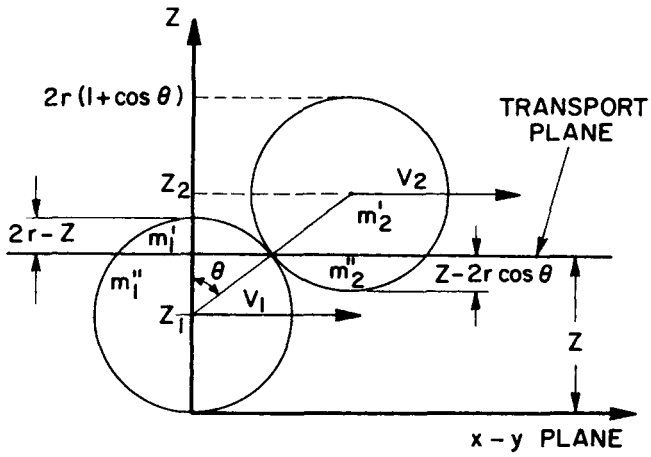


Fig. 1. Momentum transfer across plane.

It is assumed that molecule 1 loses momentum equal to mv_1 and gains momentum equal to mv_2 on every collision. (Only the case of identical, spherical molecules is considered here.) Simultaneously, molecule 2 loses momentum equal to mv_2 and gains momentum equal to mv_1.

We are interested in calculating the amount of y momentum transfer across the plane when the two molecules collide. The amount of momentum loss by part of molecule 1 above the plane is equal to m_1' and the amount gained is $m_1'v_2$, gaining a net change of $m_1'(v_2 - v_1)$. The amount of momentum loss by the part of the same molecule below the plane is $m_1''v_1$, whereas the amount gained is $m_1''v_2$, resulting in a net change of momentum equal to $m_1''(v_2 - v_1)$. Similar argument yields for the part of molecule 2 above the plane a net change in momentum equal to $m_2'(v_1 - v_2)$ and for the part below the plane, $m_2''(v_1 - v_2)$. Accordingly, the net change in momentum above the plane is $m_1'(v_2 - v_1) + m_2'(v_1 - v_2) = (m_1' - m_2')(v_2 - v_1)$, while the change below the plane is $m_1''(v_2 - v_1) + m_2''(v_1 - v_2) = (m_1'' - m_2'')(v_2 - v_1)$, per collision between molecules 1 and 2. Evidently, $(m_1' - m_2')(v_2 - v_1) + (m_1'' - m_2'')(v_2 - v_1) = 0$.

It is apparent that the momentum transport across the plane per collision is equal to $(m_1'' - m_2'')(v_2 - v_1)$, the magnitude of which is determined by the velocity difference between the two molecules $v_2 - v_1$ and by $m_1'' - m_2''$. The latter quantity is determined by the z coordinate of the plane and the orientation of the pair of molecules with respect to the plane as measured by the angle θ; that is, $m_1'' - m_2'' = m_1''(z, \theta) - m_2''(z, \theta)$. In order to obtain the momentum transfer across the plane per unit area per unit time, $(m_1'' - m_2'')(v_2 - v_1)$ must be multiplied with the number of molecule pairs $n(\theta)$ intersected by the plane per unit area and with the number of collisions f per unit time between two touching molecules, and the resulting expression averaged over the following ranges of z and θ (see Figure 1):

$$0 \leq z \leq 2r(1 + \cos\theta) \quad \text{and} \quad 0 \leq \theta \leq \pi/2 \tag{5}$$

The velocity difference between the two molecules can be written as

$$v_2 - v_1 = \frac{dv_y(z)}{dz}(2r\cos\theta) \tag{6}$$

where $\dfrac{dv_y(z)}{dz}$ may be assumed to be independent of z over the short distance of the order of a molecular diameter. The resulting momentum transfer across the plane per unit area per unit time is given by

$$f\frac{dv_y(z)}{dz}\frac{2}{\pi}\int_{\theta=0}^{\pi/2} n(\theta)\,(2r\cos\theta)\,F(\theta)\,d\theta$$

$$= f\frac{dv_y(z)}{dz}\frac{2}{\pi}(2r\cos\theta)_{\text{mean}}\int_{\theta=0}^{\pi/2} n(\theta)\,F(\theta)\,d\theta \tag{7}$$

where

$$F(\theta) = \frac{1}{2r(1+\cos\theta)}\int_{z=0}^{2r(1+\cos\theta)} \{m_1''(z,\theta) - m_2''(z,\theta)\}\,dz \tag{8}$$

and

$$\delta \equiv (2r\cos\theta)_{\text{mean}} \tag{9}$$

is, by definition, the mean distance of momentum transfer perpendicular to the plane.

It is evident from Figure 1 that one can express m_1'' and m_2'' in terms of z, θ, ϕ, and m in an elementary fashion and then evaluate the integral. In fact this has been done

by the author. There is, however, a much simpler way of obtaining the same result by writing the integral in Equation (8) as

$$\int_{z=0}^{2r(1+\cos\theta)} \{m_1''(z,\theta) - m_2''(z,\theta)\}\, dz$$

$$= \int_0^{2r} m_1''(z,\theta)dz + m\int_{2r}^{2r(1+\cos\theta)} dz$$

$$- \int_{2r\cos\theta}^{2r(1+\cos\theta)} m_2''(z,\theta)\, dz$$

$$= m\int_{2r}^{2r(1+\cos\theta)} dz \quad (10)$$

where, for reasons of symmetry, the first integral canceled with the last one.

It can be seen that the integral has been reduced to an elementary form which does not even include any reference to the shape of the colliding molecules. After substituting Equation (10) into Equation (8), one obtains

$$F(\theta) = m\frac{\cos\theta}{1+\cos\theta} \quad (11)$$

Now we proceed with evaluating Equation (7). By the assumption of random orientation of the molecule pairs, we can write that the probability for the pair to be oriented in the range of angles $d\theta$ is proportional to $\int_{\phi=0}^{2\pi} \sin\theta d\theta\, d\phi = 2\pi \sin\theta\, d\theta$; in other words we have obtained the result that $n(\theta)d\theta$ is proportional to $\sin\theta\, d\theta$. Solving Equation (7) for δ, after using Equations (9) and (11), we obtain

$$\delta = 2r\frac{\int_0^{\pi/2}\frac{\sin\theta\cos^2\theta}{1+\cos\theta}d\theta}{\int_0^{\pi/2}\frac{\sin\theta\cos\theta}{1+\cos\theta}d\theta} \quad (12)$$

The integrals in Equation (12) can be readily evaluated by making the substitution $u = 1 + \cos\theta$. The result is

$$\delta = 1.26r \quad (13)$$

The foregoing analysis has been performed for spherically shaped molecules. For nonspherical shapes the mutual orientation of the two molecules in contact needs also to be considered in addition to the orientation of the pair with respect to the plane. Unlike in the spherical case, the center-to-center distance $l(\vec{\Omega})$ between two touching molecules depends also on their mutual orientation $\vec{\Omega} \equiv (\alpha, \beta, \gamma, \ldots)$ where $\alpha, \beta, \gamma, \ldots$ are the coordinates specifying the mutual orientation. In Figure 2 the case of pear shaped bodies is shown as an illustrative example. In this case the number of components of $\vec{\Omega}$ is equal to three.

In contrast with the spherical case, for nonspherical molecules the rate of momentum transfer from one molecule to the other one may also depend on their mutual orientation $\vec{\Omega}$. Therefore, for the more general case it is necessary to introduce $p(\vec{\Omega})\ d\vec{\Omega}$, the probability of momentum transfer in the range between $\vec{\Omega}$ and $\vec{\Omega} + d\vec{\Omega}$.

For a fixed mutual orientation $\vec{\Omega}$ of the two nonspherical molecules, however, the analysis would follow along the same lines as in the spherical case. The form of the function $F(\theta)$ is the same regardless of the shape of the molecules and of $\vec{\Omega}$. Hence we can write for a fixed mutual orientation of the two molecules

$$\delta(\vec{\Omega}) = 0.63\ l(\vec{\Omega}) \quad (14)$$

where $\delta(\vec{\Omega})$ is the mean distance of momentum transfer perpendicular to the transport plane for molecule pairs of mutual orientation $\vec{\Omega}$. In order to obtain δ, Equation (14) must be averaged over all values of $\vec{\Omega}$:

$$\delta = [\delta(\vec{\Omega})]_{\text{mean}} = 0.63\ \ [l(\vec{\Omega})]_{\text{mean}} = 0.63d \quad (15)$$

where

$$d \equiv \int l(\vec{\Omega})\ p(\vec{\Omega})\ d\vec{\Omega} \quad (16)$$

is the momentum-transfer-average center-to-center distance between molecules. For brevity d will be called *molecular diameter* in liquids. Equation (15) is the generalized form of Equation (13) for molecules of any shape.

For the relatively simple case of n paraffins, Equation (16) was evaluated in a subsequent section of this paper.

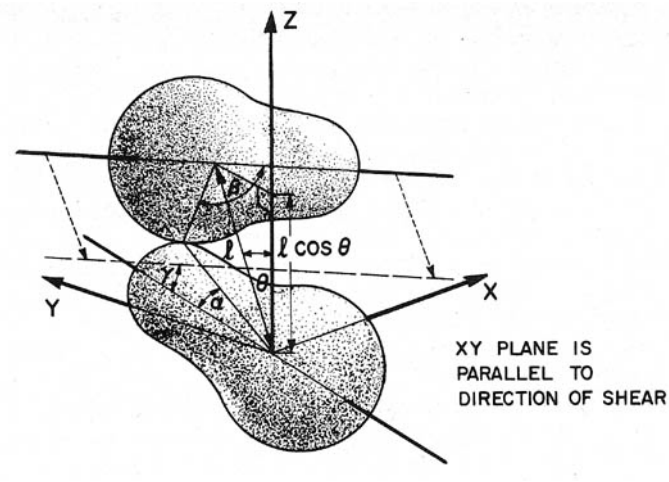


Fig. 2. Example of nonspherical molecules.

DISCUSSION OF RESULTS

Liquid Data over Wide Ranges of Temperatures

Equation (15) can be readily combined with Equation (3), resulting in a relationship between the molecular diameter on the one hand and the viscosity and the self-diffusion coefficient on the other:

$$d = 2.24\sqrt{\frac{\mu DV}{RT}} \quad (17)$$

Equation (17) has been tested in the case of all systems where the necessary data were available (see Table 1). Inspection of the results will show that all the molecular diameters calculated by Equation (17) are plausible values and show a remarkable degree of internal consistency. Direct comparison with molecular diameters obtained by different methods is inconclusive, for it is well known that different physical measurements tend to yield somewhat different values for molecular diameters (*15*). The diameters obtained for the various organic compounds are in ex-

TABLE 1. ONE-COMPONENT SYSTEMS

Liquid	Temp., °K.	μ, centipoise	Ref.	$D \times 10^5$, (sq.cm.) (sec.$^{-1}$)	Ref.	ρ, g./ml.	Ref.	$d = 2.2\sqrt{\frac{\mu DV}{RT}}$ (Å)	Comment
Argon	84.2	0.28	18	2.07	18	1.40	30	3.4	d_o = 3.4$_2$Å from gas viscosities
Mercury	296.2	1.536	29	1.67	18, 28	13.546	30	2.7$_6$	d_o = 2.8$_3$Å from gas viscosities
Methane	90.7	0.205	35	2.6	9	0.45511	35	3.5$_2$	Center to center distance CH · · · CH = 3.5Å (Fisher-Hirschfelder-Taylor molecular model)
Methane	95.2	0.176	35	3.0$_5$	9	0.44883	35	3.4$_7$	
Methane	100.0	0.153	35	3.7	9	0.44196	35	3.5	
Methane	106.1	0.132	35	4.4$_5$	9	0.43286	35	3.4$_9$	
Methane	110.5	0.121	35	5.4$_5$	9	0.42601	35	3.6$_5$	
Methane	111.1	0.119	35	5.0	9	0.42502	35	3.4$_7$	
Carbontetrachloride	293.2	0.975	19	1.18	19	1.594	22	4.7$_4$	Center to center distance CCl · · · CCl = 4.9Å (Fisher-Hirschfelder-Taylor molecular model)
Carbontetrachloride	298.2	0.902	22	1.32	26	1.584	22	4.8	
Carbontetrachloride	313.2	0.739	30	1.82	26	1.555	22	4.9$_7$	
Carbontetrachloride	323.2	0.651	30	2.00	26	1.536	22	4.8$_7$	
Carbontetrachloride	333.2	0.585	30	2.44	26	1.517	22	5.0$_3$	
Chloroform	200.0	2.2	36	0.50	37	1.662	22	4.8	
Chloroform	298.2	0.542	30	2.58	20	1.4798	22	4.7$_4$	
n-pentane	194.7	0.755	31	1.38	31	0.7155	31	5.6$_8$	d [calculated by Equation (21)] = 5.3Å
n-pentane	250.3	0.355	31	2.97	31	0.6662	31	5.2$_2$	
n-pentane	273.2	0.277	31	4.14	31	0.6453	31	5.3	
n-pentane	298.2	0.215	31	5.535	31, 25	0.6210	31	5.3	
n-pentane	308.7	0.195	31	6.29	31	0.6103	31	5.3	
n-hexane	298.2	0.2937	22	4.21	25	0.655	22	5.7	d [calculated by Equation (21)] = 5.5$_3$Å
n-heptane	194.7	2.51	31	0.415	31	0.7644	31	6.4$_8$	d [calculated by Equation (21)] = 5.7$_7$Å
n-heptane	250.3	0.702	31	1.52	31	0.7195	31	5.9$_4$	
n-heptane	273.2	0.525	31	2.08	31	0.7004	31	5.8$_6$	
n-heptane	298.2	0.386	22	3.12	25	0.6795	22	5.9$_4$	
n-heptane	305.7	0.360	31	3.22	31	0.6730	31	5.7$_2$	
n-heptane	329.7	0.282	31	4.21	31	0.6517	31	5.7$_6$	
n-heptane	353.4	0.229	31	5.76	31	0.6310	31	5.9$_6$	
n-heptane	369.0	0.202	31	6.56	31	0.6167	31	5.9	
n-octane	298.2	0.5082	22	2.25	25	0.698	22	6.1	d [calculated by Equation (21)] = 6.0$_4$Å
n-nonane	298.2	0.6621	22	1.70	25	0.71328	22	6.3$_6$	d [calculated by Equation (21)] = 6.3$_2$Å
n-decane	298.2	0.8527	22	1.31	25	0.72643	22	6.6$_2$	d [calculated by Equation (21)] = 6.6$_1$Å
n-octadecane	323.2	2.34	22	0.46	25	0.76	22	8.1	d [calculated by Equation (21)] = 8.9Å
2-methylbutane	298.2	0.219	22	5.30	38	0.615	22	5.1$_5$	d_{pentane} = 5.3Å
Neopentane	298.2	0.228	22	4.86	38	0.585	22	5.1$_7$	
3-methylpentane	298.2	0.307	22	3.61	25	0.65978	22	5.3$_8$	d_{hexane} = 5.7Å
2,3-dimethylbutane	298.2	0.361	22	3.50	25	0.65699	22	5.7$_6$	
2,2-dimethylbutane	298.2	0.351	22	3.41	25	0.64475	22	5.6$_8$	
2-methylpentane	298.2	0.295	22	3.98	38	0.650	22	5.5$_1$	
Bromoethane	303.2	0.348	22	3.96	18	1.4403	22	4.4$_8$	d (interpolated for propane) = 4.6Å
Iodoethane	292.5	0.876	17	2.212	17	1.933	22	4.6$_4$	
Iodobutane	292.5	0.876	17	1.347	17	1.615	22	5.2$_5$	d_{pentane} = 5.3Å
Benzene	288.2	0.696	22	1.87	26	0.8842	22	4.8$_2$	Mean center to center distance = 4.85Å (Fisher-Hirschfelder-Taylor molecular model)
Benzene	298.2	0.599	22	2.22	26	0.8737	22	4.8$_2$	
Benzene	308.2	0.520	22	2.59	26	0.86296	22	4.8$_1$	
Benzene	318.2	0.465	22	3.04	26	0.8522	22	4.8$_8$	
Benzene	328.2	0.415	22	3.50	26	0.8411	22	4.8$_2$	
Benzene	338.2	0.375	22	4.03	26	0.8299	22	4.9$_3$	
Benzene	373.2	0.261	36	6.15	39	0.793	40	4.9$_7$	
Benzene	423.2	0.171	36	10.0	39	0.730	40	5.0$_3$	
Benzene	473.2	0.121	36	15.0	39	0.657	40	5.1$_5$	
Benzene	523.2	0.082	36	23.9	39	0.530	40	5.6$_7$	
Benzene	561.7	0.056	36	32.7	39	0.3045	40	7.0	

TABLE 1. (Continued)

Liquid	Temp., °K.	μ, centipoise	Ref.	$D \times 10^5$, (sq.cm.) (sec.$^{-1}$)	Ref.	ρ, g./ml.	Ref.	$d = 2.2\sqrt{\frac{\mu DV}{RT}}$ (Å)	Comment
Cyclohexane	298.2	0.903	22	1.39	20	0.7738	22	5.1_7	
Bromobenzene	298.2	1.124	19	1.12	19	1.495	22	5.2	
Nitromethane	293.2	0.670	19	2.72	19	1.135	22	4.4_5	d (interpolated for ethane) = 4.2Å
Acetone	298.2	0.3075	22	4.835	20, 25	0.7851	22	4.6_8	d (interpolated for propane) = 4.6Å
p-dioxan	307.2	1.0	22	1.49	42	1.02	22	4.9_4	
Water	273.2	1.7921	30	1.1	39	0.9998	40	2.8_0	O · · · O distance in ice = 2.76Å
Water	293.2	1.0050	30	2.2	39	0.9982	40	2.8_1	
Water	298.2	0.8937	30	2.51	41	0.9970	40	2.8_1	
Water	313.2	0.6560	30	3.5	39	0.9922	40	2.8_0	
Water	333.2	0.4688	30	5.3	39	0.9832	40	2.8_3	
Water	353.2	0.3565	30	7.5	39	0.9718	40	2.8_5	
Water	373.2	0.2838	30	9.7	39	0.9583	40	2.8_5	
Water	473.2	0.133	30	23	39	0.8647	40	2.8_1	
Water	573.2	0.0896	30	44	39	0.7125	40	3.2_1	
Water	623.2	0.0728	30	61	39	0.5772	40	3.6_2	
Water	648.2	0.047	30	76	39	0.315	40	4.2_8	
Ammonia	213	0.39	36	3.8	37	0.717	40	3.1_0	
Ammonia	287	0.15	36	12.0	37	0.618	40	3.1_8	
Methanol	268.2	0.894	30	1.26	26	0.894	30	3.1_0	Center to center distance between two hydrogen bonded CH_3OH molecules ≈ 3Å
Methanol	278.2	0.747	30	1.55	26	0.747	30	3.0_5	
Methanol	288.2	0.623	30	1.91	26	0.7960	30	3.1	
Methanol	298.2	0.547	30	2.32	26	0.7865	30	3.1_7	
Methanol	308.2	0.482	30	2.71	26	0.7782	30	3.1_8	
Methanol	313.2	0.456	30	2.89	26	0.7730	30	3.1_9	
Methanol	318.2	0.428	30	3.37	26	0.7695	30	3.3_1	
Methanol	328.2	0.378	30	3.88	26	0.7601	30	3.3_1	
Ethanol	280	1.56	30	0.618	26	0.8036	22	3.4_0	d (interpolated for ethane) = 4.2Å
Ethanol	288.2	1.303	22	0.77	26	0.79367	22	3.4_2	
Ethanol	298.2	1.078	22	1.01	26	0.7851	22	3.5_2	
Ethanol	308.2	0.895	22	1.30	26	0.7766	22	3.6_2	
Ethanol	318.2	0.751	22	1.66	26	0.7676	22	3.7	
Ethanol	328.2	0.637	22	2.06	26	0.7586	22	3.7_6	
Ethanol	338.2	0.545	22	2.61	26	0.7488	22	3.8_8	
n-propanol	288.2	2.522	22	0.504	24	0.80749	22	4.4_4	d (interpolated for propane) = 4.6Å
i-propanol	288.2	2.859	22	0.474	24	0.78916	22	4.6_2	
t-butanol	308.2	2.575	22	0.497	24	0.77090	22	4.8_8	

cellent agreement with the measurements of molecular models built from Fisher-Hirschfelder-Taylor atom model kits.

The physical meaning of Equation (17) becomes clearer if the following points are considered.

1. δ as given by Equation (3) is, in general, a function both of temperature and pressure.

2. Equation (15) relates δ to the molecular diameter subject to the validity of the model of a liquid used in this paper, implying that δ is independent of the temperature and pressure.

3. As the temperature is increased, however, δ can be expected to change for two reasons: an increasing number of molecules will transport momentum in a gaslike manner by flying (jumping) across void spaces, and therefore, δ will tend to increase with the temperature; the molecular diameter will generally decrease, and, therefore, δ will also tend to decrease with increasing temperature.

It can be seen from the results in Table 1 that the two opposing effects outlined above apparently cancel each other initially, resulting in practically constant δ (and d) values over a range of temperatures above the melting point. As the temperature approaches the critical point, however, the first factor in No. 3 becomes increasingly predominant resulting in rising values of δ. At the same time, the model of liquid underlying Equations (15) and (17) starts breaking down, and the values of d calculated by Equation (17) become physically meaningless.

Example for Calculating Momentum-Transfer-Average Molecular Diameters: Normal Paraffins

The case of the six normal paraffins studied here is particularly interesting since it has been possible to calculate consistently the average diameter $[\vec{l}(\Omega)]_{\text{mean}}$ of these compounds by using the lengths and the thickness of the molecular models. In order to be able to attempt such a calculation, certain assumptions had to be made as far as the structure of these liquids and the mechanism of momentum transfer in them are concerned. It was assumed that the probability of momentum transfer in mutual orientations other than those where two paraffins molecules lie side by side is negligible. The justification for this assumption is in the fact that unless the vast majority of adjacent paraffin molecules in the liquids are very nearly side by side it is

impossible to have the experimental number densities in these liquids. In other words, there may be assumed to exist a high degree of short range order of this kind in liquid paraffins. For side by side orientations the distance l between the centers of the two molecules is (see Figure 3)

$$l(x) = \sqrt{x^2 + t^2} \tag{18}$$

where t is the thickness of the molecule and x is the distance by which the two molecules are displaced relative to each other. Using Equation (16), we can write

$$d = \int_0^{n\Delta} l(x)\ p(x)\ dx \tag{19}$$

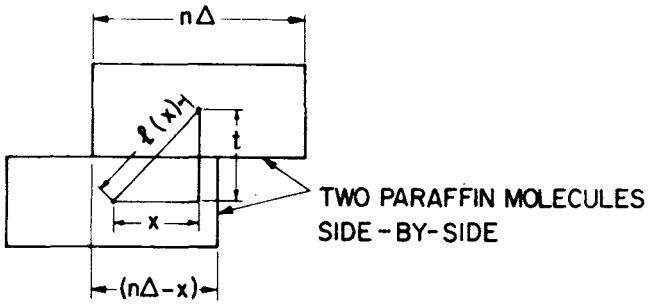
where $n\Delta$ is the length of the molecule, with n being the number of carbon atoms in the chain. There is no a priori knowledge of $p(x)$, the probability of momentum transfer between two neighboring molecules as a function of x. $p(x)$ was expressed in the following form

$$p(x) = \frac{w(x)}{\int_0^{n\Delta} w(x)\ dx} \tag{20}$$

where $w(x)$ is a weighting function giving the variation of momentum transfer with x. Probability considerations led to the use of $w(x) = (n\Delta - x)^2$. Introduction of this expression for $w(x)$ into Equation (20) and insertion of Equations (20) and (18) into Equation (19) has resulted in the following formula for the momentum-transfer-average diameter of a normal paraffin molecule:

$$d = 3t\{[1/2 - (1/8)\ (q/n)^2]\ \sqrt{(n/q)^2 + 1} + [(1/2)(q/n) - (1/8)(q/n)^3]\ \log_e [(n/q) + \sqrt{(n/q)^2 + 1}] - (5/12)(q/n)^2\ \sqrt{[(n/q)^2 + 1]^3} + (2/3)(q/n)^2\} \tag{21}$$

where $q = t/\Delta$. By substituting the values of q and t obtained from the molecular models ($q = 2.87$, $t = 4.7$Å), d was calculated for all six normal paraffins, and the results were found in excellent agreement with the values calculated from the experimental quantities (see Table 1). In the case of n-octadecane, however, Equation (21) has predicted a value for d which is about 10% too high. This is probably due to increasing deviations from the straight chain configuration in the case of longer chains.



$$d = \frac{\int_0^{n\Delta} \sqrt{x^2 + t^2}\ \left(\frac{n\Delta - x}{n\Delta}\right)^2 dx}{\int_0^{n\Delta} \left(\frac{n\Delta - x}{n\Delta}\right)^2 dx}$$

Fig. 3. Momentum transfer model for normal paraffins.

Effect of Hydrogen Bonds on the Momentum-Transfer-Average Molecular Diameters: Alcohols

The values of d obtained for the alcohols are also of special interest since they allow a study of the effect of hydrogen bonding on d.

The value of d for methanol turned out to be less than the value of d for methane, which may at first seem surprising. One possible explanation for this discrepancy is that at lower temperatures probably most of the momentum transfer takes place across the hydrogen bond, and, therefore, d is essentially the center-to-center distance between two hydrogen bonded methanol molecules at these temperatures. This distance, however, is considerably less than the mean center-to-center distance between two touching methane molecules. As the temperature is raised, the value of d is seen to increase steadily in the case of methanol and ethanol. This effect can be explained by the well-known fact that at higher temperatures hydrogen bonds tend to break down. Hence, their role in momentum transfer is also diminished relative to the role played by the alkyl radicals. It is also known that the importance of the hydrogen bond decreases with increasing chain length of alcohols. This is consistent with the results in Table 1, indicating that for the higher alcohols d approach the corresponding paraffins.

Data on Methane Extending Over a Very Wide Range of Temperatures and Pressures

Very extensive self-diffusion and viscosity data have been available on methane, making it possible to calculate δ over a wide range of temperatures and pressures both in the liquid and in the gas state. This is the only system, to this author's knowledge, where similarly extensive data are available. The self-diffusion data were determined by two independent groups of investigators, namely by Trappeniers and Oosting (*9*) and by Dawson, Khoury, and Kobayashi (*10*). The viscosity data were measured by Huang, Swift, and Kurata (*11*). The densities were determined by Trappeniers and Oosting for their own self-diffusion data; for the data of Dawson et al. the densities were calculated by using the equation of state given by Vennix and Kobayashi (*12*). The self-diffusion and viscosity data were combined by cross plotting, and δ was calculated for the various temperatures and pressures at which the self-diffusion coefficients were determined. The results have been plotted and are shown in Figure 4 as δ vs. temperature along the saturation envelope, with a few isobars and isosteres also shown.

Looking at the saturated liquid line it is apparent that δ is practically constant in the range between the freezing point and the normal boiling point; however, it gradually increases at higher temperatures and its value is about 60% greater at the critical point than at the melting point. The horizontal dashed line is the relationship between d and δ [Equation (15)] extended all the way up to the critical temperature.

The other dashed line was calculated by using the elementary kinetic theory expression

$$\delta = 2/3\ \frac{1}{\sqrt{2}_v\ \pi d^2} \tag{22}$$

The value for d used in this equation was the same as obtained by Equation (17) at the freezing point of methane. It is remarkable that this ideal value of δ for gaseous methane appears to approach asymptotically the experimental saturated vapor line. The two dashed lines intersect very nearly at the critical temperature.

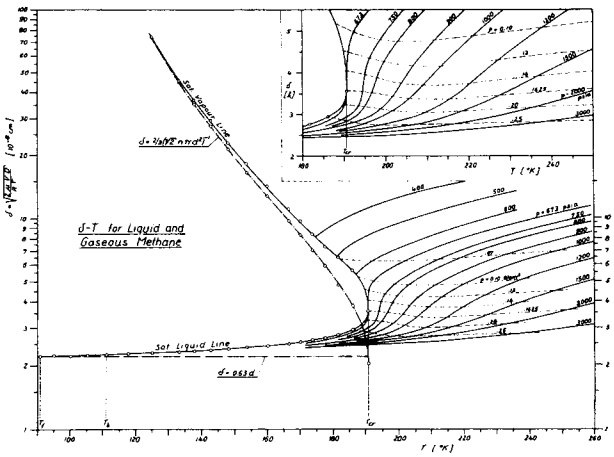


Fig. 4. Momentum transfer distance chart for methane.

The supercritical isobars appear to have a point of inflection at about the critical density isostere, suggesting the possibility of a higher order phase transition in this region. Such a transition has been considered among others by Bernal (*8*), who suggested that one basic difference between a liquid and a gas is that in the liquid the molecules form a coherent structure (continuum) with the voids being discontinuous, whereas in the gas it is the molecules that are discontinuous and the space between them forms a continuum. According to this picture, such a difference might exist even in the supercritical region, and the behavior of the isobars in Figure 4 would suggest that at the point of inflection the number of bonds broken in the coherent structure of the liquid per unit degree change in temperature is the greatest.

Prediction of Self-Diffusion Coefficients of Liquids

Inspection of Figure 4 suggests a possibility of calculating liquid transport coefficients from measurements made in the gas state and vice versa. By assuming that at low pressures Equation (22) is valid for the gas, this expression can be equated to Equation (2) written for the gas. The resulting relationship can be solved for d, and if the same molecular diameter is applicable to the liquid as to the gas, then d can be eliminated between this equation and Equation (17) giving

$$\frac{\mu_l V_l D_l}{T_l} = 2.65 \times 10^{-14} \sqrt{\frac{V_g T_g}{\mu_g D_g}} \qquad (23)$$

Use of the experimental values of μ_g and D_g for a low pressure gas would seem to permit calculation of D_l for the liquid at temperatures not far from the melting point.

Use of the Chapman-Enskog method (*13*) of predicting D_g and μ_g, however, results in temperature dependent values of d

$$d = 0.747 \times 10^{-8}\, \sigma\, (\Omega_D \Omega_V)^{1/4} \qquad (24)$$

because the generalized collision integrals Ω_D and Ω_V increase with decreasing temperature. It follows from this that the two curves for δ of the saturated vapor should not become identical, in contradiction with the behavior of the experimental data on methane. Therefore, prediction of self-diffusion coefficients of liquids from gas data by Equations (24) and (17) does not seem possible.

Inspection of Figure 4 shows that the $\delta = 2/3\lambda$ curve for the saturated vapor intersects with the $\delta = 0.63d$ line for the saturated liquid at about the critical temperature. One obtains the following expression for d at the point of intersection of the two lines:

$$d = \left(2/3 \frac{V_c}{0.63 \sqrt{2}\, \pi N} \right)^{1/3} \qquad (25)$$

This equation suggests that the molecular diameter can be expected to be proportional to the cube root of the critical volume of the substance. Combination of Equation (25) with Equation (17) results in the following simple relation:

$$\frac{\mu V D}{RT} = 0.107 \times 10^{-16}\, V_c^{2/3} \qquad (26)$$

By plotting $\mu VD/RT$ vs. the 2/3 power of the critical volume for all substances where the necessary liquid data were available, a straight line passing through the origin of slope 0.124 has been found with a mean deviation of $\pm$ 4% (see Figure 5). The only two compounds badly off the line are the two lower alcohols, methanol and ethanol. For these two substances the group $\mu VD/RT$ is strongly temperature dependent also at temperatures below the normal boiling point. In the case of ethanol, its value increases by about 32% from 280° to 338°K. As it has been discussed in more detail in the previous section, this behavior is due to the gradual breakdown of the hydrogen bonds. It is fair to say that Equation (26) and also Equation (1) can be expected to offer only very crude approximations in the case of ethanol and methanol.

The reason for the 16% discrepancy between the theoretical and the best empirical values of the numerical coefficient in Equation (26) is most likely to be found in the treatment of d as a constant quantity. In actual fact d varies with temperature, and for better results its temperature dependence should be taken into account.

The values of the molecular diameter at the critical temperature for the kinetic theory model of the gas have been calculated by Equation (24). The results were generally in good agreement with the values calculated by Equation (25) and were consistently lower by 8%, on the average, than the diameters obtained by Equation (17) for the model of the liquid between the melting point and the normal boiling point; that is

$$(d_l)_{\text{melting point}} \simeq 1.08 d_c \qquad (27)$$

The difference between the theoretical and the empirical values of the numerical coefficient in Equation (26) is about 16% which corresponds to $(d_l)^2_{m.p.}/d_c^2$ by Equation (27).

If Equation (24) is applied at the critical temperature and combined with Equations (17) and (27), one obtains

$$\frac{\mu VD}{RT} = 0.129 \times 10^{-16}\, \sigma^2\, (\Omega_D \Omega_V)_{T_c}^{1/2} \qquad (28)$$

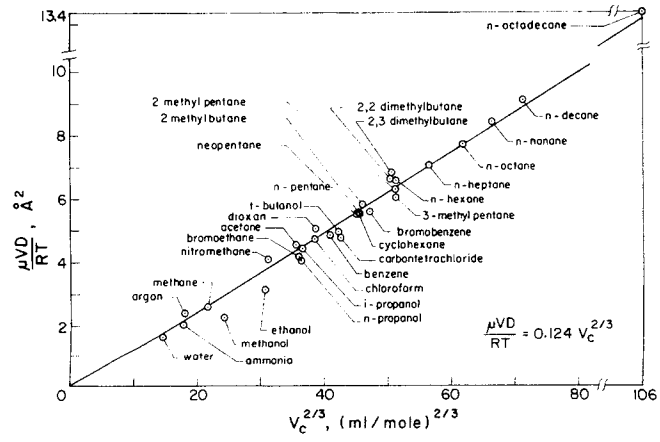


Fig. 5. Self-diffusivity correlation for liquids.

Equation (28) predicts self-diffusion coefficients in liquids with an average deviation even somewhat less than Equation (26) (with the coefficient 0.124 instead of 0.107).

The mean deviation either of Equation (26) or (28) is considerably better than that of the existing equations known to the author, and it is comparable to the accuracy of many self-diffusion data used in this study. Further improvement in the predictive power of Equation (28) might be expected if the ratio d_l/d_c were calculated individually for each liquid from intermolecular potential functions.

The data contained in Table 1 were also tested in the form $\mu D/RT$ vs. $V^{-1/3}$ [see Equation (1)], resulting in an average deviation of about $\pm$ 10%, in agreement with the findings of others (*43, 44*). Equation (26) is markedly more accurate than the older correlation in the case of nonspherical and polar organic molecules.

Comparison of Equations (26) and (28) suggests the possibility of a correlation for critical volumes in terms of T_c and Lennard-Jones parameters.

CONCLUSIONS

1. By using the relation between transport coefficients of pure fluids and a molecular-kinetic-model of liquids an equation has been derived between macroscopic transport properties and effective molecular diameters in liquids. The diameters are momentum-transfer-average values.

2. Effective molecular diameters have been calculated for six *n*-paraffins from the lengths and the thickness of the molecules. The results were in good agreement with the values obtained from transport properties.

3. Hydrogen bonds have been found to reduce the value of effective molecular diameters.

4. The molecular-kinetic-model of liquids used in this work is analogous to the elementary kinetic theory model of gases. At the critical temperature the two models are equivalent. Combination of the two at T_c has resulted in a predictive equation for self-diffusion coefficients of liquids in terms of the critical volume, with a mean deviation of $\pm$ 4%. For nine nonspherical and/or polar organic liquids, the average deviation was 2.4% compared with about 12% obtained by existing correlations.

5. Application of the relation between transport coefficients of pure fluids to gases has resulted in an equation to calculate molecular diameters in gases as a function of temperature. Using this equation at the critical temperature and combining it with the equation for molecular diameters in liquids, we get another correlation for self-diffusion coefficients of liquids in terms of Lennard-Jones potential parameters. This correlation is, on the average, somewhat better than one with the critical volume. It could be improved even more by calculating the variation with temperature of the molecular diameters in the liquids.

ACKNOWLEDGMENTS

The author wishes to express his thanks for N.R.C. Operating Grant, and a grant from the University of Waterloo Research Fund, which made this study possible. Thanks are due to a number of colleagues, including D. S. Scott, K. C. Chang, G. D. Wedlake, Horst Ertl, and J. R. Barney for their help in this work.

NOTATION

D = self-diffusion coefficient
D_{AA}, D_{BB} = tracer diffusion coefficients in a binary solution
d = molecular diameter
$F(\theta)$ = function defined by Equation (8)
f = collision frequency
k = Boltzmann constant
$l(\vec{\Omega})$ = center-to-center distance betwen two touching molecules of mutual orientation $\vec{\Omega}$
m = molecular mass
N = Avogadro number
N_A, N_B = mole fractions in a binary solution
n = number of carbon atoms in a normal paraffin molecule
$n(\theta)$ = number of molecular pairs of orientation θ intersected by the plane per unit area
$p(\vec{\Omega})$ = probability of momentum transfer between two touching molecules as a function of $\vec{\Omega}$
q = t/Δ
R = universal gas constant
r = radius of a spherical molecule
T = absolute temperature
t = thickness of a normal paraffin chain
V = molecular volume
V_c = critical volume
v, $v_y(z)$ = y velocity component
$w(x)$ = weighting function defined on page 11
x, y, z = Cartesian coordinates

Greek Letters

α, β, γ = generalized coordinates
δ = mean distance of momentum transfer perpendicular to the transport plane
Δ = length of a chain segment in a normal paraffin molecule
θ, ϕ = spherical polar coordinates
λ = mean free path
μ = viscosity
ν = number density for a gas in Equation (22)
σ = Lennard-Jones distance parameter
τ_{zy} = y momentum transfer in the z direction per unit area per unit time
Ω_D Ω_V = generalized collision integrals for diffusion and for viscosity
$\vec{\Omega}$ = $(\alpha, \beta, \gamma, \ldots)$ mutual orientation vector of two touching molecules
ω = solid angle

Subscripts

g = gas
l = liquid

Subscripts

1 = molecule No. 1
2 = molecule No. 2

Superscripts

$'$ = part of a molecule above the plane
$''$ = part of a molecule below the plane

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Manuscript received March 16, 1971; revision received May 6, 1971; paper accepted May 19, 1971.

Thermodynamics of Nearly-Ideal Systems

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The industrial importance of mixtures of closely similar substances is out of proportion to their relatively small numbers due to their frequent occurrence and the difficulty of their separations. A procedure specially designed for the general prediction of their properties, particularly relative volatility, over a wide range of state variables is needed.

Such a procedure is developed in this work for convenient application to multicomponent systems with the use of generalized functions. The relative volatility of a nearly ideal system is decomposed into ideal solution factors and nonideality factors. The first order perturbation theory of Longuet-Higgins is adopted for the calculation of the nonideality factor. The validity of the procedure for the quantitative description of real mixtures is demonstrated with the system propane/propylene for which extensive data are available.

The required pure fluid properties for the general application of the procedure are reviewed. System parameters are evaluated for 15 binary systems of industrial interest.

A great deal of effort has been devoted to the phase behavior and other properties of close boiling mixtures (*1* to *23*). Almost invariably the experimental work is difficult due to the closeness of the vapor and liquid compositions in an equilibrium cell. The resulting correlation of the data is usually specific for the given system over the range of variables studied (*8, 12, 15, 20*). Efforts of such lim-

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