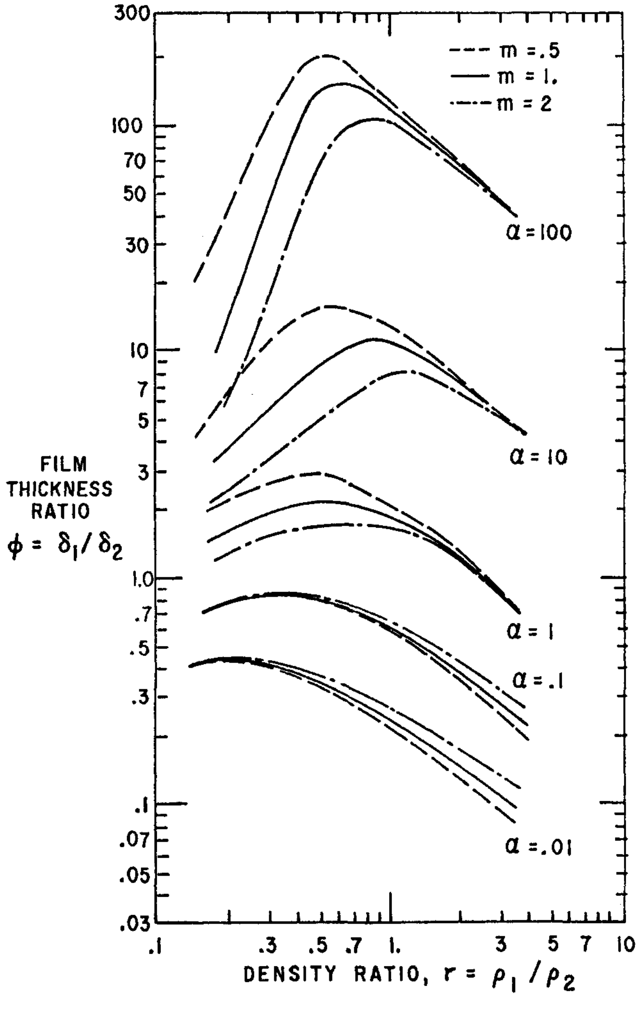

Fig. 1. Film thickness ratio for two immiscible falling films in laminar flow.

$$G_2 = 1 + 3\varphi/m + 3r\varphi^2/m \qquad (11)$$

The mass flow rates per unit width, $\Gamma = \bar{v}\,\delta\rho$, are

$$\Gamma_i = \frac{\rho_i^2 g_y \delta_i^3}{3\mu_i}\,G_i \qquad (12)$$

and the ratio of the film thickness from Equations (10), (11), and (12) is given by

$$\varphi^3 + 1.5\,[(m\gamma)^{2/3}\,r^{-7/3} - \gamma r^{-1}]\,\varphi^2 - 3\,r^{-2}\varphi - (m\gamma)r^{-2} = 0 \qquad (13)$$

Thus, the film thickness ratio is a function of the ratios of densities, viscosities, and mass flow rates but not of the gravitational force.

Equation (13) was solved numerically, using a digital computer, for a number of combinations of physical properties and flow rates. The results are shown in Figure 1. For given mass flow rates, the ratio of the film thicknesses passes through a maximum at a given density ratio. The viscosity ratio contribution reverses with increased density ratio.

Figure 1 or Equation (13) may be used to determine the average velocities or the mass flow rates from Equations (9) to (12). On the other hand, if the mass flow rates are known, one can calculate the individual film thicknesses and the average velocities. In addition to the above assumptions, the analysis neglects the effects of surface tension.

This analysis was developed in conjunction with a study of film-by-film condensation of immiscible liquids. The subsequent heat transfer treatment parallels that of Nusselt.

ACKNOWLEDGMENT

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NOTATION

g_y = gravitational force in y direction
G_i = correction in Equation (9) for component i
m = μ_1/μ_2, viscosity ratio
r = ρ_1/ρ_2, density ratio
v_i = velocity of component i
x = distance away from wall

Greek Letters

δ_i = film thickness component i
γ = Γ_1/Γ_2, ratio of mass flow rates
Γ_1 = mass flow rate per unit width for component i
φ = δ_1/δ_2, film thickness ratio
ρ_i = density of component i
μ_i = viscosity of component i

Free Volume Theory for Self-Diffusivity of Simple Nonpolar Liquids

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In a recent paper (*1*), hereafter referred to as I, it has been shown that the Macedo-Litovitz equation (2),

$$\eta = A_o T^{1/2} \exp\left(\frac{V_o}{V - V_o}\right) \exp\left(\frac{E_v}{RT}\right) \qquad (1)$$

provides a good description of the effects of temperature and pressure on liquid viscosity of simple liquids for $\rho \geqq 2\rho_c$, provided that the temperature dependence of V_o and the density dependence of E_v are accounted for. By arguments analogous to those of Macedo and Litovitz, a similar equation may be written for the self-diffusion coefficient,

$$D = B_o T^{1/2} \exp\left(-\frac{V_o(T)}{V - V_o(T)}\right) \exp\left(-\frac{E_v(V)}{RT}\right) \qquad (2)$$

In this paper we test Equation (2) for liquids composed of monatomic and quasispherical polyatomic molecules. According to Equations (1) and (2), V_o and E_v should be the same for viscosity and self-diffusion coefficient at a particular temperature and density. The quantity V_o was therefore obtained from Equations (3), (4), and (5a) of paper I (assuming $n = 12$ in the 6, n potential), and E_v was obtained from curve A of Figure 4 in paper I. The remaining parameter B_o was evaluated by comparing experimental data with Equation (2), using the computer.

Tables 1 and 2 show the data sources and parameters for the fluids studied, while Figure 1 illustrates the agreement for methane. Values of ϵ/k, T_m, V_m and V_c used were those of table 2 in paper I. Unfortunately no

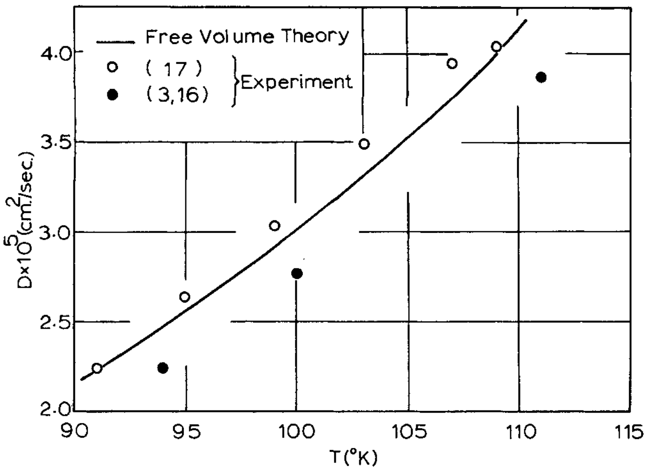

Fig. 1. Test of free volume theory for self-diffusion coefficient of saturated liquid methane.

measurements of self-diffusivity seem to have been made at constant volume, and there appears to be no data for simple fluids at high pressure. Naghizadeh and Rice (*3*) report data for the inert gas liquids for pressures above atmospheric, but the pressure range covered is not sufficient for a significant change in density to occur. Most of the data tested in Table 2 are thus for saturated liquids.

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NOTATION

A_o = pre-exponential factor in viscosity equation
B_o = pre-exponential factor in self-diffusivity equation
D = self-diffusion coefficient
E_v = activation energy per mole
k = Boltzmann constant
M = molecular weight
n = repulsion exponent in $(6, n)$ potential
R = gas constant
T = temperature
T_m = melting temperature
V = molal volume
V_c = critical volume
V_m = melting volume
V_o = minimum free volume per mole needed for molecular flow to occur
V_o^1 = value of V_o when $kT/\epsilon = 1$

Table 1. Data Sources and Range of Conditions

Molecule	Temperature range (°K.)	Molal volume range (cc. mole^{-1})	Density reference	Self-Diffusivity reference	Number of points
Ar	85-110	28-31	*8, 9*	*3, 14*	16
Kr	110-160	33-41	*10*	*3*	8
Xe	168-208	43-48	*10, 11*	*3*	12
CO	69-78	33-35	*10, 12*	*15*	4
CH_4	91-145	35-43	*10, 12*	*3, 16, 17*	10
CF_4	88-123	45-52	*13*	*17*	10

The average percentage errors of about 15% shown in Table 2 are substantially larger than those for viscosity. However, the data for self-diffusion coefficients of simple liquids are of relatively low accuracy, and discrepancies between different workers in excess of this figure are common (*3, 4*). The theories of Eyring (*5*), Weymann (*6*), and Cohen and Turnbull (*7*) give explicit expressions for B_o, and suggest that the group $(B_oM^{1/2}/V_m^{1/3})$ may be approximately the same for different molecules. Table 2 indicates some fluctuation for this group. However the method of fitting B_o was not highly sensitive, because of the small range of density and temperature over which D values have been measured. This behavior is similar to that observed for A_o in the viscosity equation (*1*). The factors A_o and B_o may be obtained from a single measurement of viscosity and self-diffusion coefficient respectively, and Equations (1) and (2) then used to predict the transport coefficients at other temperatures and pressures.

Table 2. Parameters for Molecules Studied

Molecule	V_o^1 (cc. mole^{-1})	10^5B_o (sq. cm. sec.$^{-1}$ °K.$^{-1/2}$)	$\dfrac{B_oM^{1/2}}{V_m^{1/3}} \cdot 10^5$	Average % Error
Ar	15.50	1.83	3.81	15.3
Kr	19.02	1.39	3.92	17.8
Xe	24.55	1.66	5.41	14.3
CO	18.34	3.14	5.17	5.9
CH_4	19.5	2.91	3.55	9.0
CF_4	25.2	0.50	1.31	12.9

ϵ = energy parameter in $(6, n)$ potential
η = viscosity
ρ = density
ρ_c = critical density

LITERATURE CITED

1. Gubbins, K. E., and M. J. Tham, *AIChE J.*, **15**, 264 (1969).
2. Macedo, P. B., and T. A. Litovitz, *J. Chem. Phys.*, **42**, 245 (1965).
3. Naghizadeh, J., and S. A. Rice, *ibid.*, **36**, 2710 (1962).
4. Yen, W. M. and R. E. Norberg, *Phys. Rev.*, **131**, 269 (1963).
5. Glasstone, S., K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," Chapt. 9, McGraw-Hill, New York (1941).
6. Weymann, H., *Kolloide Zeit.*, 138, 41 (1954).
7. Cohen, M. H., and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
8. Zhdanova, N. F., *Soviet Phys. JETP.*, **4**, 749 (1957).
9. Van Itterbeek, A., O. Verbeke, and K. Staes, *Physica*, **29**, 742 (1963).
10. Boon, J. P., J. C. Legros, and G. Thomaes, *ibid.*, **33**, 547 (1967).
11. Reynes, E. G., and G. Thodos, *ibid.*, **30**, 1529 (1964).
12. Johnson, V. J., *WADD Tech. Rept. 60-56*, Wright-Patterson Air Force Base, Ohio (1960).
13. Reed, T. M., "Fluorine Chemistry," J. H. Simons, ed., Vol. 5, Chapt. 2, Academic Press, New York (1963).
14. Corbett, J. W., and J. H. Wang, *J. Chem. Phys.*, **25**, 422 (1956).
15. Cini-Castagnoli, G., *Physica*, **30**, 953 (1964).
16. Gaven, J. V., J. S. Waugh, and W. H. Stockmayer, *J. Chem. Phys.*, **38**, 287 (1963).
17. Rugheimer, J. H., and P. S. Hubbard, *ibid.*, **39**, 552 (1963).