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A Predictive Equation for the Tracer Diffusion of Various Solutes in Gases, Supercritical Fluids, and Liquids

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A predictive equation for the infinitely dilute diffusion coefficients of various solutes in gaseous and liquid phases is proposed. The expressions proposed previously for the tracer diffusion in binary hard sphere fluids are examined critically and a new expression, based on the molecular dynamics simulations of Alder et al. (1974), obtained. The obtained expression is extended first to a Lennard–Jones fluid and then, by introducing a coupling factor, to a real fluid. The molecular diameter and energy parameters used in the equation are calculated with generalized correlations and simple combining rules. The coupling factor is correlated with the acentric factor. The derived equation is tested against a large number of experimental data: 1443 points for 120 systems, including the diffusions of various solutes in gases, supercritical fluids, and liquids. Excellent predictions were obtained: the total absolute average deviation is only 8.42%. For most systems, the predicted errors are comparable to the experimental uncertainties.

Introduction

The infinitely dilute diffusion coefficient of a solute in a solvent is one of the most important transport properties. In some industrial processes, such as those encountered in supercritical fluid (SCF) extraction, the systems can be considered simply as infinitely dilute. For most concentrated liquid mixtures, the diffusion coefficients can be estimated on the basis of the tracer (infinitely dilute) diffusivities of each of the components, using the Darken (1948), the Vignes (1966), or any other of the equations reviewed recently by Pertler et al. (1996). For this reason, numerous equations have been suggested for this property.

For gaseous systems at low densities, the kinetic theory of Enskog provides reasonable estimations of the diffusion coefficient (Hirschfelder et al., 1964; Chapman and Cowling, 1970). For dense fluids, however, no acceptable theory is available even for the simple hard sphere (HS) fluid. The equations used for design are mostly empirical or semi-empirical.

For the infinitely dilute diffusion coefficient in a liquid solvent, the empirical Wilke–Chang (Wilke and Chang, 1955) equation and its modifications are usually employed. Semi-empirical expressions based on the Lennard–Jones (LJ) fluid have been more recently suggested (Salim and Trebble, 1995; Liu et al., 1997). The equation has the following form:

$$D_{12}^{\infty} = D_{12}^{\text{LJ}}(\rho_2, T; \sigma_{12}^{\text{LJ}}, \epsilon_{12}^{\text{LJ}}/k) \quad (1)$$

where D_{12}^{∞} represents the infinitely dilute diffusion coefficient of solute 1 in solvent 2, ρ_2 is the number density of the solvent molecules, T is the temperature (in K), and σ_{12}^{LJ} and $\epsilon_{12}^{\text{LJ}}/k$ are the binary molecular diameter and energy parameters, respectively, which can be evaluated from those of the pure substances using some combining rules. However, the predictions of eq 1 are not satisfactory. At least one of the molecular

parameters, σ_{12}^{LJ} or $\epsilon_{12}^{\text{LJ}}/k$, had to be adjusted to fit the experimental data. For instance, the geometrical mean which was usually employed had to be replaced by

$$\epsilon_{12}^{\text{LJ}}/k = (1 - I_{12})[(\epsilon_{11}^{\text{LJ}}/k)(\epsilon_{22}^{\text{LJ}}/k)]^{1/2} \quad (2)$$

where I_{12} is an adjustable parameter which was regressed from diffusion data. However, the parameter I_{12} could not be related to the nature of the system (Salim and Trebble, 1995; Liu et al., 1997). The other models for liquid systems, such as the free volume models (Dymond, 1985), can be used only for correlation purposes, again because the fitted parameters cannot be related to the nature of the system (Liu et al., 1997).

Regarding the SCF systems, various methods have been adopted to predict the tracer diffusion coefficient (Liong et al., 1991). Some of them are based on a Stokes–Einstein type equation (Sun and Chen, 1986), and others contain two terms, one of the Stokes–Einstein form and another one which accounts for the singular behavior near the critical point (Liu and Ruckenstein, 1997). Many authors developed equations based on the rough hard sphere (RHS) theory (Chen, 1983; Erkey and Akgerman, 1989a,b; Erkey et al., 1990; Catchpole and King, 1994; Akgerman et al., 1996; Eaton and Akgerman, 1997). The basic equation, eq 3, which is similar to that proposed by Chandler (1975) for pure fluids, was suggested by Bertucci and Flygare (1975):

$$D_{12}^{\infty} \approx D_{12}^{\text{RHS}} = A_D D_{12}^{\text{HS}}(\rho_2, \sigma_{12}) \quad (3)$$

In eq 3, $D_{12}^{\text{HS}}(\rho_2, \sigma_{12})$ is the tracer diffusion coefficient in a hard sphere fluid, and A_D is the translational–rotational coupling factor due to the nonsphericity of the molecules. The predictive capability of eq 3 is limited by the fact that A_D is temperature-dependent (Dymond, 1985; Erkey and Akgerman, 1989a,b). To improve the correlation, the molecular diameter, σ_{12} , was also considered temperature-dependent (Akgerman et al., 1996; Eaton and Akgerman, 1997).

The goal of this paper is to extend our recent equation for the self-diffusion coefficient (Ruckenstein and Liu, 1997) to the tracer diffusion coefficient of solutes in various fluids. The paper is organized as follows. In the next section the expressions proposed previously for the tracer diffusion in binary hard sphere fluids will be

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examined and a new equation based on the molecular dynamics simulations of Alder et al. (1974) suggested. In the third section, the new equation for the HS fluid is transformed to one for a Lennard–Jones fluid and finally to one for a “real” fluid. The parameters needed for prediction are correlated with the critical constants and the acentric factor. The obtained equation is tested against a large number of experimental data: 1443 points for 120 diverse systems. The results are discussed in the fourth section and the conclusions are summarized in the last one.

Expressions for Hard Sphere Fluids

Background. As noted previously (Dymond, 1985; Ruckenstein and Liu, 1997), the expression for the HS fluid plays a key role in an equation for self-diffusivity. This observation is true for binary systems as well. The expression for a HS fluid can be written as a modification of the Enskog equation:

$$D_{12}^{\text{HS}} \equiv \left(\frac{D_{12}^{\text{HS}}}{D_{12}^{\text{E}}} \right) D_{12}^{\text{E}} \equiv F_{12} D_{12}^{\text{E}} \quad (4)$$

where D_{12}^{E} is given by

$$D_{12}^{\text{E}} = \frac{3}{8\rho_2\sigma_{12}^2} \left(\frac{kT}{2\pi m_{12}} \right)^{1/2} \frac{1}{g(\sigma_{12})} \quad (5)$$

In eq 5, $g(\sigma_{12})$ is the radial distribution function at contact for an infinitely dilute solution, and m_{12} (in kg) is related to the masses of the molecules of the pure substances, m_1 and m_2 , via the following equation:

$$m_{12} \equiv \frac{m_1 m_2}{m_1 + m_2} = \frac{0.001 M_1 M_2}{N_a (M_1 + M_2)} \quad (6)$$

where M_i ($i = 1, 2$) is the molecular weight in g/mol and N_a is the Avogadro number.

Generally, one can write the following expression:

$$F_{12} = F_{12}(\rho_2^*, \sigma_1/\sigma_2, m_1/m_2) \quad (7)$$

where the reduced density ρ_2^* is defined as

$$\rho_2^* \equiv \rho_2 \sigma_2^3 = N_a \sigma_2^3 / V_2 = \sqrt{2} V_0 / V_2 \quad (8)$$

and V_2 is the molar volume of the solvent and V_0 the closed-packed molar volume of the solvent ($V_0 = N_a \sigma_2^3 / \sqrt{2}$).

Obviously, for self-diffusion, F_{12} reduces to F_{22} :

$$\lim_{\substack{\sigma_1/\sigma_2=1 \\ m_1/m_2=1}} F_{12} = \frac{D_{22}^{\text{HS}}}{D_{22}^{\text{E}}} \equiv F_{22}(\rho_2^*) \equiv F_{22} \quad (9)$$

Various expressions have been proposed for $F_{22}(\rho_2^*)$ which are summarized elsewhere (Ruckenstein and Liu, 1997). Speedy (1987), using the molecular dynamics (MD) simulations of Easteal et al. (1983, 1984), suggested the following empirical expression:

$$F_{22}(\rho_2^*) = g(\sigma_{22})(1 - \rho_2^*/1.09)(1 + 0.4\rho_2^{*2} - 0.83\rho_2^{*4}) \quad (10)$$

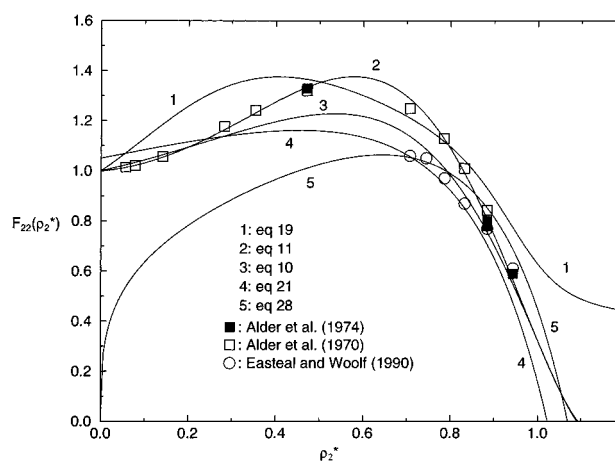


Figure 1. Plot of $F_{22}(\rho_2^*) (= D_{22}^{\text{HS}}/D_{22}^{\text{E}})$ against the reduced density ρ_2^* .

where $g(\sigma_{22})$ is the radial distribution function at contact for the pure solvent. In our previous paper (Ruckenstein and Liu, 1997), another expression was obtained by using the MD simulations of Alder et al. (1970) and Erpenbeck and Wood (1991):

$$F_{22}(\rho_2^*) = 1 + 0.94605\rho_2^{*1.5} + 1.4022\rho_2^{*3} - 5.6898\rho_2^{*5} + 2.6626\rho_2^{*7} \quad (11)$$

Equation 11 should be preferred to eq 10 because the two simulations on which the former is based are consistent with each other and inconsistent with the simulations of Easteal et al. (1983, 1984) on which the latter is based. In addition, as shown previously (Ruckenstein and Liu, 1997), the expression for the diffusion coefficient of a LJ fluid based on eq 11 provides more accurate results than that based on eq 10.

At low densities, the following requirement must be satisfied to recover the Enskog theory:

$$\lim_{\rho_2^* \rightarrow 0} F_{22}(\rho_2^*) = 1 \quad (12)$$

At high densities, the MD simulations of Woodcock (1981a,b) indicated that $F_{22}(\rho_2^*)$ should approach zero for $\rho_2^* = \rho_s^* \approx 1.1$:

$$\lim_{\rho_2^* \rightarrow \rho_s^*} F_{22}(\rho_2^*) = 0 \quad (13)$$

As shown in Figure 1, both eqs 10 and 11 satisfy the above two constraints. However, in the middle-density range the two expressions provide different results.

A constraint similar to eq 12 should be also satisfied by F_{12} :

$$\lim_{\rho_2^* \rightarrow 0} F_{12}(\rho_2^*, \sigma_1/\sigma_2, m_1/m_2) = 1 \quad (14)$$

since the Enskog theory holds at low densities. In what follows, eqs 9, 12–14 will be used to test the expressions proposed in the literature for F_{12} . A new expression for F_{12} , which reduces to eq 11 for pure substances and satisfies all the above constraints, is proposed.

Analysis of the Expressions for F_{12} Proposed in Literature. Sung and Stell (1984) derived the follow-

ing equation for the diffusion coefficient in infinitely dilute solutions for a hard sphere fluid:

$$F_{12} = \left(\frac{1 + \gamma_B \frac{\sigma_2}{\sigma_1}}{1 + \gamma \frac{\sigma_2}{\sigma_1}} \right)^2 \frac{g(\sigma_{12})}{1 + 4\eta_2 g(\sigma_{22})} + \frac{1 + \frac{\sigma_2}{\sigma_1} \frac{D_{12}^H}{D_{12}^E}}{1 + \gamma \frac{\sigma_2}{\sigma_1} \frac{D_{12}^H}{D_{12}^E}} \quad (15)$$

where

$$\eta_2 = \frac{1}{6} \pi \rho_2^* = \frac{0.7405 V_0}{V_2} \quad (16)$$

and γ and γ_B ($\gamma_B = \lim_{\rho_2 \rightarrow 0} \gamma$) are given by the following equation:

$$\frac{1}{(1 - \gamma^3 \eta_2)} \left(1 - \gamma^3 \eta_2 + \frac{2\gamma^3 \eta_2}{1 + \gamma \sigma_2 / \sigma_1} \right) \left(1 - \gamma^3 \eta_2 + \frac{\gamma^3 \eta_2}{1 + \gamma \sigma_2 / \sigma_1} \right) = 1 + \frac{4\eta_2(1 - 0.5\eta_2)}{(1 - \eta_2)^3} \quad (17)$$

The first term in eq 15 represents the Enskog limit, while the second the hydrodynamic limit. The ratio D_{12}^H/D_{12}^E in the second term is given by (Sun and Chen, 1985a):

$$\frac{D_{12}^H}{D_{12}^E} = 2.881 \left(1 + \frac{\sigma_1}{\sigma_2} \right) \left(1 + \frac{m_2}{m_1} \right)^{-1/2} \frac{\eta_2 g(\sigma_{12})}{\mu_2^{\text{HS}}/\mu_0} \quad (18)$$

where μ_2^{HS}/μ_0 is the ratio of the viscosities of a HS solvent and a perfect gas.

For a pure solvent, eq 15 combined with 18 leads to

$$F_{22} = \left(\frac{1 + \gamma_B^0}{1 + \gamma^0} \right)^2 \frac{g(\sigma_{22})}{1 + 4\eta_2 g(\sigma_{22})} + \frac{8.15 \eta_2 g(\sigma_{22})}{(1 + \gamma^0) \mu_2^{\text{HS}}/\mu_0} \quad (19)$$

where the superscript "0" refers to the pure solvent and $\gamma_B^0 = 1.1909$ (γ^0 should be calculated from eq 17 for the pure solvent).

Equations 15 and 19 satisfy the zero density constraint, eqs 14 and 12, respectively. As shown in Figure 1, eq 19 provides quantitative agreement with the MD simulations of Alder et al. (1970) in the dilute and middle-density ranges. At high densities, it leads, however, to nonzero values, and hence it does not satisfy the constraint eq 13.

Table 1 and Figures 2 and 3 present the calculated values of F_{12} given by eq 15 and compare them with the MD simulations of Alder et al. (1974). One can see that the agreement is poor. For this reason, eq 15 will not be used further. While Sun and Chen (1985a) employed eq 15 for the SCF systems, the agreement with experimental data is most likely due to the two empirical parameters used to express the temperature-dependence of the molecular diameter, which strongly affects the diffusion coefficient.

In another paper, Sun and Chen (1985b) proposed an expression for F_{12} (eq 20) on the basis of the MD simulations of Herman and Alder (1972) and Alder et

Table 1. MD Data and Calculation Results for $F_{12} = D_{12}^{\text{HS}}/D_{12}^E$

σ_1/σ_2	m_1/m_2	ρ_2^*	MD ^a	eq 32	eq 15	eq 20	ref for MD data
1.00	1.00	0.4714	1.33	1.33	1.40	1.16	<i>b</i>
1.00	0.10	0.4714	0.82	0.80	1.00	0.70	<i>b</i>
1.00	0.01	0.4714	0.39	0.39	0.81	0.33	<i>b</i>
1.00	1/5625	0.4714	0.19	0.20	0.73	0.08	<i>b</i>
0.75	1.00	0.4714	1.27	1.35	1.24	1.16	<i>b</i>
0.75	0.10	0.4714	0.91	0.87	0.93	0.70	<i>b</i>
0.75	0.01	0.4714	0.58	0.53	0.77	0.33	<i>b</i>
0.75	1/5625	0.4714	0.38	0.45	0.70	0.08	<i>b</i>
0.50	1.00	0.4714	1.22	1.32	1.09	1.23	<i>b</i>
0.50	0.10	0.4714	0.99	0.96	0.84	0.75	<i>b</i>
0.50	0.01	0.4714	0.79	0.74	0.72	0.35	<i>b</i>
0.50	1/5625	0.4714	0.75	0.74	0.67	0.09	<i>b</i>
0.25	1.00	0.4714	1.13	1.08	0.93	1.61	<i>b</i>
0.25	0.10	0.4714	1.06	1.04	0.76	0.99	<i>b</i>
0.25	0.01	0.4714	1.00	1.04	0.67	0.47	<i>b</i>
0.25	1/5625	0.4714	1.03	1.03	0.64	0.12	<i>b</i>
1.00	1.00	0.8839	0.78	0.81	0.95	0.71	<i>b</i>
1.00	0.10	0.8839	0.40	0.47	0.71	0.33	<i>b</i>
1.00	0.01	0.8839	0.14	0.11	0.59	0.11	<i>b</i>
0.75	1.00	0.8839	0.83	0.86	0.82	0.79	<i>b</i>
0.75	0.10	0.8839	0.47	0.50	0.63	0.40	<i>b</i>
0.75	0.01	0.8839	0.15	0.15	0.54	0.15	<i>b</i>
0.50	1.00	0.8839	0.94	0.93	0.68	0.93	<i>b</i>
0.50	0.10	0.8839	0.61	0.61	0.55	0.50	<i>b</i>
0.50	0.01	0.8839	0.35	0.32	0.49	0.20	<i>b</i>
0.50	1/5625	0.8839	0.13	0.14	0.46	0.03	<i>b</i>
0.25	1.00	0.8839	1.08	1.13	0.54	1.33	<i>b</i>
0.25	0.10	0.8839	0.93	0.98	0.46	0.75	<i>b</i>
0.25	0.01	0.8839	0.75	0.80	0.41	0.32	<i>b</i>
0.25	1/5625	0.8839	0.69	0.69	0.40	0.06	<i>b</i>
1.00	1.00	0.9428	0.59	0.57	0.79	0.48	<i>b</i>
1.00	0.10	0.9428	0.35	0.37	0.63	0.16	<i>b</i>
1.00	0.01	0.9428	0.12	0.12	0.55	0.01	<i>b</i>
0.75	1.00	0.9428	0.67	0.64	0.68	0.61	<i>b</i>
0.75	0.10	0.9428	0.36	0.38	0.56	0.27	<i>b</i>
0.75	0.01	0.9428	0.15	0.15	0.51	0.07	<i>b</i>
0.50	1.00	0.9428	0.76	0.70	0.57	0.80	<i>b</i>
0.50	0.10	0.9428	0.49	0.48	0.49	0.40	<i>b</i>
0.50	0.01	0.9428	0.26	0.27	0.45	0.14	<i>b</i>
0.50	1/5625	0.9428	0.12	0.12	0.43	0.01	<i>b</i>
0.25	1.00	0.9428	0.93	0.91	0.46	1.23	<i>b</i>
0.25	0.10	0.9428	0.80	0.80	0.41	0.67	<i>b</i>
0.25	0.01	0.9428	0.71	0.67	0.38	0.27	<i>b</i>
0.25	1/5625	0.9428	0.56	0.55	0.37	0.05	<i>b</i>
1.00	4.00	0.4714	1.56	1.62	1.58	1.19	<i>c</i>
1.00	1.00	0.4714	1.34	1.33	1.40	1.16	<i>c</i>
1.00	0.25	0.4714	1.07	1.01	1.14	0.91	<i>c</i>
1.00	0.01	0.4714	0.40	0.39	0.81	0.33	<i>c</i>
1.00	1/5625	0.4714	0.24	0.20	0.73	0.08	<i>c</i>
1.00	4.00	0.8839	1.02	1.05	1.06	0.81	<i>c</i>
1.00	1.00	0.8839	0.80	0.81	0.95	0.71	<i>c</i>
1.00	0.25	0.8839	0.57	0.63	0.80	0.48	<i>c</i>
1.00	0.01	0.8839	0.12	0.11	0.59	0.11	<i>c</i>
grand AAD				4.97	75.62	34.51	

^a The extrapolated MD data for the infinite size system. ^b Alder et al. (1974). ^c Herman and Alder (1972).

al. (1974) in the following ranges: $0.5 < \sigma_1/\sigma_2 < 1.6$, $0.5 < m_1/m_2 < 4.0$, and $1.5 < V_2/V_0 < 3.0$.

$$F_{12} = 1.0514 \left(\frac{\sigma_{12}^2}{\sigma_1 \sigma_2} \right) \left(\frac{2}{1 + m_2/m_1} \right)^{1/2} g(\sigma_{12}) \left(\frac{m_2}{m_1} \right)^{0.167} \times \left[1 - 0.9779 \rho_2^* \left(\frac{m_2}{m_1} \right)^{0.0165} \left(\frac{\sigma_1}{\sigma_2} \right)^{0.129} \right] \quad (20)$$

For a pure solvent, eq 20 reduces to

$$F_{22}(\rho_2^*) = 1.0514 g(\sigma_{22}) (1 - 0.9779 \rho_2^*) \quad (21)$$

The predictions provided by eq 21 are also presented in

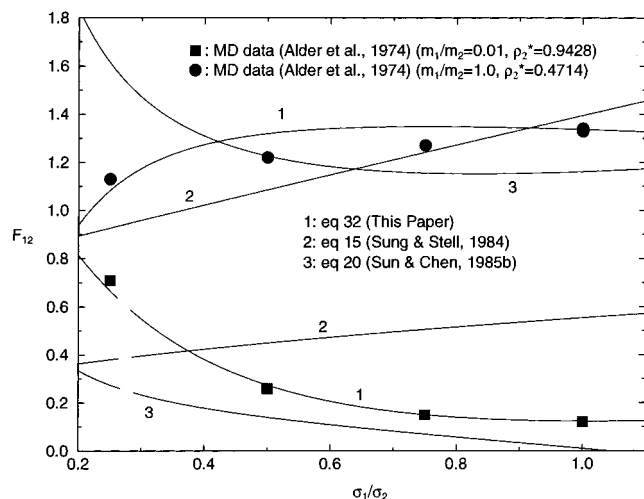


Figure 2. Plot of F_{12} ($= D_{12}^{\text{HS}}/D_{12}^{\text{E}}$) against the molecular size ratio σ_1/σ_2 .

Figure 1. While eq 21 satisfies approximately the constraints at both zero (with a slightly different numerical factor, 1.0514) and high densities, it provides too low values in the middle-density range. As shown by eqs 10 and 11, the ratio $F_{22}/g(\sigma_{22})$ cannot be a linear function of density. Consequently, eqs 20 and 21 are not expected to provide reasonable values for F_{12} and F_{22} . Table 1 and Figures 2 and 3 present the calculated results.

Easteal and Woolf (1990) carried out MD simulations for tracer diffusion coefficients in HS systems and proposed the following empirical expression for the molecular-weight ratio dependence of F_{12}/F_{22} :

$$\ln\left(\frac{F_{12}}{F_{22}}\right) = a_0 + a_1 \ln\left(\frac{m_1}{m_2}\right) + a_2 \left[\ln\left(\frac{m_1}{m_2}\right)\right]^2 \quad (22)$$

where the coefficients, a_0 , a_1 , and a_2 are dependent on both the density ρ_2^* and the molecular size ratio σ_1/σ_2 .

On the basis of the MD simulations of Easteal and Woolf (1990), Salim and Trebble (1995) proposed the following expressions for the coefficients in eq 22:

$$a_0 = -1.02564\rho_2^{*4} \ln\left(\frac{\sigma_1}{\sigma_2}\right) \quad (23)$$

$$a_1 = -0.24107 + 1.27589h_{12} - 1.35439h_{12}^2 + 0.62393h_{12}^3 \quad (24)$$

$$a_2 = -0.056 \quad (25)$$

where $h_{12} = \rho_2^{*2} \ln(\sigma_1/\sigma_2)$.

For F_{22} , Salim and Trebble (1995) used the expression of Speedy (1987), eq 10, which, being based on the MD simulations of Easteal et al. (1983, 1984), is consistent with the MD simulations for mixtures (Easteal and Woolf, 1990). Nevertheless, one can easily see that because of eqs 24 and 25, eq 22 does not satisfy the constraint eq 14.

More recently, Eaton and Akgerman (1997) proposed the following expression, on the basis of the MD simulations of Easteal and Woolf (1990):

$$\frac{V_2(D_{12}^{\text{HS}})}{V_0(D_{12}^{\text{E}})} = a \left[\left(\frac{V_2}{V_0} \right)^\alpha - b_{12} \right] \quad (26)$$

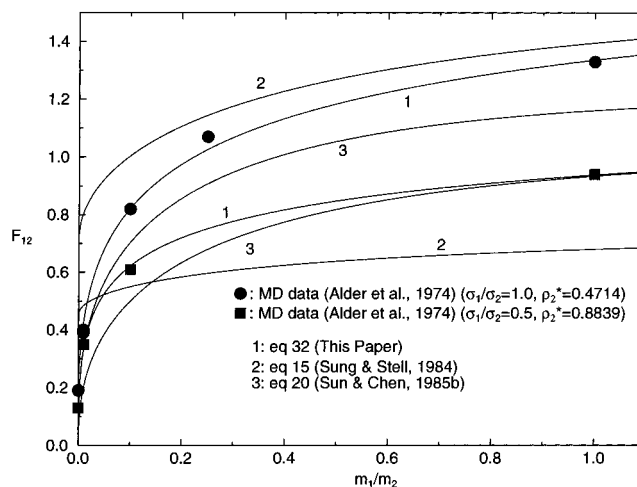


Figure 3. Plot of F_{12} ($= D_{12}^{\text{HS}}/D_{12}^{\text{E}}$) against the molecular weight ratio m_1/m_2 .

where

$$\alpha = \frac{\sigma_2}{\sigma_1} - \frac{1}{3} \quad (27a)$$

$$b_{12} = \left(\frac{m_2}{m_1}\right)^{0.03587} \left[0.6001 + 0.8491 \left(\frac{\sigma_2}{\sigma_1}\right) - 0.244 \left(\frac{\sigma_2}{\sigma_1}\right)^2 \right] \quad (27b)$$

and a is a function of the molecular size ratio σ_1/σ_2 . Using the MD simulations of Easteal and Woolf (1990), we obtained

$$a = 1.689(\sigma_1/\sigma_2)^{2.0674} \quad (27c)$$

For a pure solvent, eq 26 reduces to

$$F_{22}(\rho_2^*) = 1.1943g(\sigma_{22})(1.26\rho_2^{*1/3} - 1.2052\rho_2^*) \quad (28)$$

An obvious shortcoming of eq 28 is that it predicts $F_{22} = 0$ at zero density instead of 1. For this reason, eq 26 is valid only in the high-density range (see Figure 1).

A New Expression for F_{12} . Considering the limitations of the expressions summarized above, we propose an expression for F_{12} on the basis of the MD simulations of Herman and Alder (1972) and Alder et al. (1974). These simulations for binary HS mixtures are preferred to those of Easteal and Woolf (1990), because, as already noted, the recent MD simulations carried out by Erpenbeck and Wood (1991) for pure HS fluids are consistent with those of the former and inconsistent with those of the latter authors.

As shown by Alder et al. (1974), the dependence of F_{12} on σ_1/σ_2 is complex. At low densities, F_{12} increases as σ_1/σ_2 increases when $m_1/m_2 = 1$, while it decreases with increasing σ_1/σ_2 when $m_1/m_2 \leq 0.1$; at high densities, F_{12} always decreases as σ_1/σ_2 increases. Instead of using a form which simply contains ρ_2^* , σ_1/σ_2 , and m_1/m_2 as variables, as in the previous empirical correlations, eqs 20, 22, and 26, some terms involved in the theoretical expressions of Sung and Stell (1984) and Alder et al. (1974) will also be included.

The theoretical expression of Sung and Stell (1984) (eq 15) suggests that F_{12} should depend on the radial

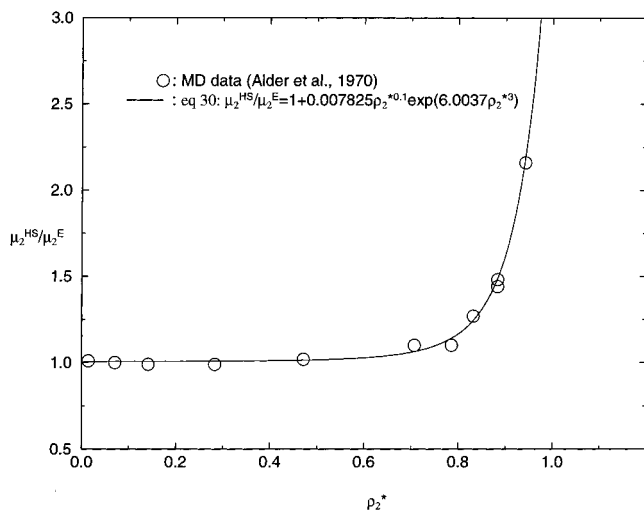


Figure 4. Ratio of the viscosities for the hard sphere and Enskog fluids, $\mu_2^{\text{HS}}/\mu_2^{\text{E}}$, against the reduced density ρ_2^* .

distribution functions at contact and on the viscosity ratio, μ_2^{HS}/μ_0 , given by

$$\frac{\mu_2^{\text{HS}}}{\mu_0} = \frac{\mu_2^{\text{HS}}}{\mu_2^{\text{E}}} [1/g(\sigma_{22}) + 3.2\eta_2 + 12.18\eta_2^2 g(\sigma_{22})] \quad (29)$$

where $\mu_2^{\text{HS}}/\mu_2^{\text{E}}$ is the ratio between the hard sphere and Enskog viscosities of the solvent. On the basis of the MD simulations of Alder et al. (1970) for an HS fluid, we obtained the expression

$$\frac{\mu_2^{\text{HS}}}{\mu_2^{\text{E}}} = 1 + 0.007825(\rho_2^*)^{0.1} \exp(6.0037\rho_2^{*3}) \quad (30)$$

which represents well the MD simulations (see Figure 4).

Alder et al. (1974) introduced a hydrodynamic vortex effect in F_{12} characterized by the ratios σ_1/σ_2 and m_1/m_2 and by the quantity Δ :

$$\Delta = \frac{[\mu_2^{\text{HS}}/\mu_0 + 1.2/g(\sigma_{22})]^{3/2}}{[\mu_2^{\text{HS}}/\mu_0 + 1.2(m_2/2m_1)^{1/2}(\sigma_{22}/\sigma_{12})^2 g^{-1}(\sigma_{12})]^{3/2}} \quad (31)$$

Consequently, F_{12} is expected to depend not only on σ_1/σ_2 , m_1/m_2 , and the solvent density but also on the radial distribution functions at contact, the viscosity ratio, μ_2^{HS}/μ_0 , and the quantity Δ . After a long number of trials, the following expression was selected:

$$\frac{F_{12}}{F_{22}} = 1.0 + \sum_{i=1}^{10} b_i G_i \quad (32)$$

where the b_i 's are constants and G_i 's are functions listed in Table 2. The simulations of Alder et al. (1974) indicate logarithmic dependences on the ratios σ_1/σ_2 and m_1/m_2 . In addition, the density dependence should satisfy the constraints at low and high densities. For these reasons, most of the G_i 's contain logarithmic factors of one or both of the above ratios and some contain the density factor $\rho_2^{*0.01}$. The effects of the viscosity ratio, the radial distribution functions at contact, and the quantity Δ are taken into account in

Table 2. Functions and Coefficients in Equation 32^a

i	b_i	G_i
1	-0.293977	$\chi \ln(\sigma_1/\sigma_2)$
2	-0.106089	$\chi [\ln(\sigma_1/\sigma_2)]^2 \ln(m_1/m_2)$
3	0.111318	$\chi \ln(m_1/m_2)$
4	0.002865	$\ln(\mu_2^{\text{HS}}/\mu_0) [\ln(m_1/m_2)]^2$
5	-0.0069724	$\chi \ln(m_1/m_2) (\sigma_2/\sigma_1)^{0.5}$
6	-0.0020652	$\chi \ln(\sigma_1/\sigma_2) (m_2/m_1)^{0.5}$
7	3.21576	$\{\ln[g(\sigma_{22})/g(\sigma_{12})]\}^2$
8	-0.334952	$\chi \ln \Delta$
9	-0.26190	$\chi [\ln(\sigma_1/\sigma_2)]^2 (m_2/m_1)^{1/6}$
10	0.143989	$\delta(\sigma_1/\sigma_2, m_1/m_2) \ln(\mu_2^{\text{HS}}/\mu_2^{\text{E}})$

$$^a \chi \equiv (\rho_2^*)^{0.01}; \delta(\sigma_1/\sigma_2, m_1/m_2) = \begin{cases} 0, & (\sigma_1/\sigma_2) \text{ and } (m_1/m_2) = 1.0 \\ 1, & (\sigma_1/\sigma_2) \text{ or } (m_1/m_2) \neq 1.0 \end{cases}$$

some of the G_i 's. Equation 11 was used for F_{22} . Equation 32 satisfies all the constraints noted in a previous section.

Throughout this paper, the Carnahan–Starling expression (Carnahan and Starling, 1969) for the radial distribution function was adopted for the pure solvent

$$g(\sigma_{22}) = \frac{1 - 0.5\eta_2}{(1 - \eta_2)^3} \quad (33)$$

and the Mansoori et al. expression (1971) for the radial distribution function of a binary mixture with a solute at infinite dilution

$$g(\sigma_{12}) = (1 - \eta_2)^{-3} \left(1 - \eta_2 + \frac{2\eta_2}{1 + \sigma_2/\sigma_1} \right) \times \left(1 - \eta_2 + \frac{\eta_2}{1 + \sigma_2/\sigma_1} \right) \quad (34)$$

Another expression for $g(\sigma_{12})$, proposed by Alder et al. (1974), provided the same results.

The results obtained on the basis of eq 32 are listed in Table 1 along with the MD data. The MD data provided by Alder et al. (1974), extrapolated to an infinite number of molecules, were employed. One can see from Table 1 that eq 32 can accurately represent the MD data over wide ranges of molecular size and weight ratios; eqs 15 and 20 provide unsatisfactory results. Only a few points for $m_1/m_2 = 1/5625$ were disregarded since the values of F_{12} were too small (less than 0.02) and their simulation uncertainties comparable to those values (Alder et al., 1974).

Figure 2 illustrates the dependence of F_{12} on σ_1/σ_2 . A comparison between the MD data (Alder et al., 1974) and those calculated using three different expressions is also included in the Figure. One can see that the theory of Sung and Stell (1984) (eq 15) and the empirical expression of Sun and Chen (1985b) (eq 20) provide wrong trends under some conditions.

Figure 3 presents the dependence of F_{12} on m_1/m_2 and shows that eq 15 (Sung and Stell, 1984) overestimates F_{12} at high values of σ_1/σ_2 and underestimates it at low values of σ_1/σ_2 . Equation 20 (Sun and Chen, 1985b) always underestimates F_{12} .

Due to the range of the MD data used in obtaining our eq 32, this equation is recommended for calculating F_{12} in the following ranges: density, ρ_2^* , from 0.0 to 0.95; molecular size ratios, σ_1/σ_2 , from 0.25 to 1.0; and molecular weight ratios, m_1/m_2 , from 0.0002 to 4.0.

Table 3. MD Simulations and Summary of Expressions for $F_{12} = D_{12}^{HS}/D_{12}^E$

MD Simulations				
author	ρ^*	σ_1/σ_2	m_1/m_2	NDP
Herman and Alder (1972)	0.4714–0.8839	1.0	1/5625–4.0	10
Alder et al. (1974)	0.4714–0.9428	0.25–1.0	1/5625–1.0	48
Easteal and Woolf (1990)	0.7071–0.9428	0.5–1.0	0.100–5/3	360

Expressions			
author	expression	no. of eqs	MD data used
Sung and Stell (1984)	theoretical	eqs 15–18	Herman and Alder (1972), Alder et al. (1974) Easteal and Woolf (1990) Easteal and Woolf (1990) Easteal and Woolf (1990) Herman and Alder (1972), Alder et al. (1974)
Sun and Chen (1985b)	correlation	eq 20	
Easteal and Woolf (1990)	correlation	eq 22	
Salim and Trebble (1995)	correlation	eqs 22–25	
Eaton and Akgerman (1997)	correlation	eqs 26–27	
this paper	correlation	eq 32	

Table 4. Data for Pure Substances

substance	M	T_C (K)	P_C (bar)	V_C (cm ³ /mol)	ω	σ_L^a (Å)	ε_L/k^b (K)
argon	39.948	150.80	48.70	74.90	0.001	3.32544	119.75
krypton	83.800	209.40	55.00	91.20	0.005	3.63836	166.28
helium	3.017	3.31	1.14	72.90	−0.473	3.29557	2.63
hydrogen	2.016	33.00	12.90	64.30	−0.216	3.16052	26.21
xenon	131.30	289.70	58.40	118.40	0.008	3.96910	230.05
nitrogen	28.013	126.20	33.90	89.80	0.039	3.53276	100.21
carbon monoxide (CO)	28.010	132.90	35.00	93.20	0.067	3.57679	105.53
carbon dioxide (CO ₂)	44.010	304.19	72.85	94.07	0.239	3.58789	241.55
carbon disulfide	76.131	552.00	79.00	160.00	0.109	4.21440	438.34
methane	16.043	190.40	46.00	99.20	0.011	3.65196	151.20
ethylene (C ₂ H ₄)	28.054	282.40	50.40	130.40	0.089	4.00050	224.25
ethane	30.070	305.40	48.80	148.30	0.099	4.17576	242.52
propane	44.094	369.80	42.50	203.00	0.153	4.63647	293.66
<i>n</i> -pentane	72.151	469.70	33.70	304.00	0.251	5.30453	372.98
<i>n</i> -hexane	86.178	507.50	30.10	370.00	0.299	5.66356	403.00
cyclohexane (C ₆ H ₁₂)	84.162	554.15	40.40	311.70	0.212	5.34894	440.05
<i>n</i> -heptane	100.205	540.30	27.40	432.00	0.349	5.96371	429.05
<i>n</i> -octane	114.232	568.80	24.90	492.00	0.398	6.22793	451.68
<i>n</i> -nonane	128.259	594.60	22.90	543.00	0.445	6.43609	472.17
<i>n</i> -decane	142.286	617.70	21.20	603.00	0.489	6.66491	490.51
<i>n</i> -undecane	156.313	638.80	19.70	660.00	0.535	6.86863	507.27
<i>n</i> -dodecane	170.340	658.20	18.20	713.00	0.575	7.04777	522.67
<i>n</i> -tetradecane	198.394	693.00	14.40	830.00	0.581	7.41392	550.31
<i>n</i> -hexadecane (C ₁₆ H ₃₄)	226.448	722.00	14.10	944.00	0.742	7.73890	573.33
2,3-dimethylbutane (DMB)	86.178	500.00	31.30	358.00	0.247	5.60165	397.05
benzene	78.115	562.20	48.90	259.00	0.212	5.02869	446.44
toluene	92.141	591.80	41.00	316.00	0.263	5.37342	469.94
ethylbenzene	106.168	617.20	36.00	374.00	0.302	5.68389	490.11
<i>n</i> -propylbenzene	120.195	638.20	32.00	440.00	0.344	6.00030	506.79
isopropylbenzene	120.195	631.10	32.10	440.00	0.326	6.00030	501.15
<i>m</i> -xylene	106.168	617.10	35.40	376.00	0.325	5.83406	490.03
<i>p</i> -xylene	106.168	616.20	35.10	379.00	0.320	5.84953	489.32
<i>o</i> -xylene	106.168	630.30	37.30	369.00	0.310	5.65845	500.52
mesitylene	120.195	664.50	34.50	480.00	0.366	6.17688	527.67
hexachlorobenzene	284.780	847.70	32.28	557.50	0.568	6.49287	673.15
phenol	94.113	694.20	61.30	229.00	0.438	4.82652	551.26
benzoic acid	122.124	752.00	45.60	341.00	0.620	5.51155	597.16
2-naphthol	144.170	811.40	47.40	375.50	0.594	5.69148	644.33
naphthalene	128.174	748.40	40.50	413.00	0.303	5.87497	594.30
phenanthrene	178.200	873.00	33.30	554.00	0.517	6.47926	693.24
pyrene	202.260	907.48	30.73	619.50	0.612	6.72516	720.62
chrysene	228.290	990.83	27.41	701.50	0.641	7.00967	786.81
caffeine	194.200	855.60	41.50	488.00	0.906	6.21101	679.43
C4:0 ethyl ester	116.200	579.00	31.40	400.00	0.417	5.81267	459.78
C8:0 ethyl ester	172.300	655.70	21.18	621.50	0.670	6.73239	520.69
C10:0 ethyl ester	200.000	699.30	17.88	733.50	0.761	7.11468	555.31
C14:0 ethyl ester	256.430	788.40	13.23	957.50	0.897	7.77562	626.06
C16:0 ethyl ester	284.480	835.00	11.56	1069.5	0.926	8.06768	663.07
C18:0 ethyl ester	312.500	883.40	10.19	1181.5	0.934	8.34001	701.50
C22:0 ethyl ester	368.700	987.80	8.081	405.50	0.957	8.83688	784.40
C18:2 methyl ester	294.500	884.00	12.05	1065.5	0.902	8.05761	701.98
C20:5 ethyl ester	356.500	823.40	11.34	1137.5	0.824	8.23517	653.86
C22:6 methyl ester	342.500	852.40	10.35	1229.0	0.851	8.45031	676.88
C22:6 ethyl ester	356.500	867.10	11.02	1285.0	0.860	8.57676	688.56
chlorotrifluoromethane (CClF ₃)	104.459	302.00	38.70	180.40	0.198	4.45760	239.82
carbon tetrachloride (CCl ₄)	153.823	556.40	45.60	275.90	0.193	5.13577	441.83
sulfur hexafluoride (SF ₆)	146.054	318.70	37.60	198.80	0.286	4.60427	253.08
acetonitrile	41.053	545.50	48.30	173.00	0.327	4.32559	433.18
acetone	58.080	508.10	47.00	209.00	0.304	4.68171	403.48
ethyl acetate	88.107	523.20	38.30	286.00	0.362	5.19769	415.47

^a Calculated with eq 46. ^b Calculated with eq 47.

Table 5. Systems Employed and Calculation Results

system (solute + solvent)	T_{r2}	ρ_{r2}	NDP	prediction		correlation		ref
				A_D^{hh}	AAD	A_D^{ji}	AAD	
Diffusion in Gases								
argon + helium	74.9698–97.6284	0.0362–0.2740	16	0.9827	2.04	0.9631	1.07	<i>a</i>
nitrogen + helium	74.9698–97.6284	0.0362–0.2740	12	0.9856	1.39	0.9958	1.01	<i>a</i>
CO ₂ + helium	74.9698–97.6284	0.0362–0.2297	16	0.9965	10.04	0.9055	0.80	<i>a</i>
methane + helium	74.9698–97.6284	0.0362–0.2740	16	0.9835	9.32	1.0844	1.25	<i>a</i>
CO ₂ + ethylene	1.0559–1.2330	0.0514–1.5935	49	0.9889	5.94	1.0203	5.51	<i>b</i>
ethylene + CO ₂	0.9803–1.1447	0.0365–1.6886	48	0.9880	7.45	1.0405	6.77	<i>b</i>
Diffusion in SCF								
naphthalene + ethylene	1.0097–1.1266	0.8160–2.3935	20	0.9833	8.69	1.0023	8.79	<i>c,d</i>
<i>n</i> -pentane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.2020	7.87	1.1142	3.92	<i>e</i>
<i>n</i> -hexane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.2112	3.79	1.2018	3.60	<i>e</i>
<i>n</i> -heptane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.2614	3.50	1.2612	3.50	<i>e</i>
<i>n</i> -octane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.2936	3.87	1.3011	3.86	<i>e</i>
<i>n</i> -nonane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.3259	4.02	1.3255	4.02	<i>e</i>
<i>n</i> -decane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.3574	4.06	1.3577	4.05	<i>e</i>
<i>n</i> -undecane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.3918	4.78	1.4011	4.78	<i>e</i>
<i>n</i> -dodecane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.4228	6.74	1.4156	6.61	<i>e</i>
<i>n</i> -tetradecane + CO ₂	0.9834–1.0130	1.5620–1.7482	5	1.4276	9.97	1.3319	8.12	<i>e</i>
benzene + CO ₂	0.9834–1.0952	0.7481–2.0009	67	0.9784	8.97	0.9453	8.54	<i>e,f–j</i>
toluene + CO ₂	1.0063–1.0952	1.1564–2.0009	34	0.9736	5.42	1.0214	4.10	<i>g,i,k</i>
ethylbenzene + CO ₂	1.0295–1.0952	1.2977–2.0009	15	0.9696	4.08	1.0103	1.99	<i>g</i>
<i>n</i> -propylbenzene + CO ₂	1.0295–1.0952	0.7652–2.0009	26	0.9650	8.93	0.9652	8.91	<i>g</i>
isopropylbenzene + CO ₂	1.0295–1.0952	1.2977–2.0009	15	0.9670	4.49	1.0119	2.13	<i>g</i>
mesitylene + CO ₂	0.9966–1.0952	1.0901–1.8810	7	0.9625	9.58	1.0628	3.36	<i>f,h</i>
hexachlorobenzene + CO ₂	1.0125–1.0783	0.8550–1.9237	14	0.9350	8.98	0.9763	7.05	<i>l</i>
phenol + CO ₂	1.0125–1.0783	0.7032–1.7185	21	0.9535	8.63	0.8747	7.80	<i>k</i>
benzoic acid + CO ₂	0.9823–1.0477	1.1483–1.8359	7	0.9267	13.26	1.0675	2.67	<i>m</i>
2-naphthol + CO ₂	1.0132–1.0461	1.6284–1.9284	5	0.9309	34.10	0.6925	4.12	<i>n</i>
naphthalene + CO ₂	0.9151–1.0952	0.8567–2.2820	76	0.9695	11.96	0.9869	11.63	<i>c,d,h,l,o</i>
phenanthrene + CO ₂	0.9966–1.0952	0.8550–1.9237	21	0.9426	14.04	1.0832	6.06	<i>h,l</i>
pyrene + CO ₂	0.9966–1.0952	1.3893–1.8810	3	0.9266	16.87	1.1115	4.37	<i>h</i>
chrysene + CO ₂	0.9966–1.0952	1.7100–1.8810	4	0.9232	13.55	1.0952	1.98	<i>h</i>
caffeine + CO ₂	1.0125–1.0783	0.9127–1.7228	21	0.8724	6.21	0.8718	6.20	<i>k</i>
acetone + CO ₂	0.9834–1.0952	1.0508–1.8888	36	0.9694	7.57	0.9688	7.57	<i>e,h,p,q</i>
ethyl acetate + CO ₂	1.0125–1.0783	0.4553–1.7228	15	0.9629	19.99	0.8146	19.13	<i>k</i>
C4:0 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	16	0.9562	4.99	0.9938	4.23	<i>r</i>
C8:0 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	16	0.9183	6.37	0.9740	3.70	<i>r</i>
C10:0 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	16	0.9018	8.77	0.9851	4.70	<i>r</i>
C14:0 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	16	0.8743	12.01	0.09901	5.03	<i>r</i>
C16:0 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	17	0.8680	11.56	0.9785	4.48	<i>r</i>
C18:0 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	17	0.8662	12.53	0.9872	4.86	<i>r</i>
C22:0 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	17	0.8611	18.30	1.0498	5.29	<i>r</i>
C18:2 methyl ester + CO ₂	1.0132–1.0789	1.5796–1.9857	19	0.8732	6.74	0.9360	1.44	<i>s</i>
C20:5 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	17	0.8895	7.07	0.9490	4.97	<i>r</i>
C22:6 methyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	17	0.8840	10.16	0.9813	4.43	<i>r</i>
C22:6 ethyl ester + CO ₂	1.0125–1.0454	1.2825–1.8168	17	0.8821	11.24	0.9909	4.64	<i>r</i>
<i>p</i> -xylene + CClF ₃	1.0535–1.0535	0.6908–1.7270	8	0.9720	28.11	0.7511	8.45	<i>t</i>
acetone + CClF ₃	1.0535–1.0535	0.6873–1.6510	10	0.9736	14.89	0.8456	3.82	<i>t</i>
CCl ₄ + SF ₆	1.0292–1.0292	0.6806–1.9056	6	0.9758	17.63	0.8267	4.89	<i>t</i>
benzene + SF ₆	1.0292–1.0292	0.6806–1.9056	8	0.9740	4.83	0.9555	4.26	<i>t</i>
toluene + SF ₆	1.0292–1.0292	0.5445–1.9056	11	0.9688	3.78	0.9378	2.61	<i>t</i>
<i>p</i> -xylene + SF ₆	0.8885–1.0610	0.6806–2.2459	51	0.9623	6.44	0.9085	5.98	<i>t</i>
mesitylene + SF ₆	1.0292–1.0292	0.6806–1.9056	10	0.9567	6.37	0.9048	4.34	<i>t</i>
naphthalene + SF ₆	0.9984–1.0298	1.5089–2.0278	5	0.9643	8.36	0.9635	8.35	<i>n</i>
benzoic acid + SF ₆	1.0292–1.0612	1.2485–1.9065	6	0.9188	19.89	0.7656	2.33	<i>n</i>
benzene + DMB	1.0464–1.0964	1.4320–1.9084	11	0.9777	2.07	0.9586	1.25	<i>u</i>
toluene + DMB	1.0464–1.0964	1.4320–1.9084	10	0.9728	2.61	0.9478	1.33	<i>u</i>
naphthalene + DMB	1.0464–1.0964	1.4320–1.9084	9	0.9686	4.28	0.9287	1.20	<i>u</i>
phenanthrene + DMB	1.0464–1.0964	1.4320–1.9084	11	0.9415	6.48	0.8840	1.29	<i>u</i>
Diffusion in Liquids								
argon + cyclohexane	0.5380–0.7504	2.4147–2.8666	7	0.9944	16.65	0.8483	5.73	<i>v</i>
krypton + cyclohexane	0.5380–0.7504	2.4147–2.8666	7	0.9942	8.56	1.0828	5.20	<i>v</i>
xenon + cyclohexane	0.5380–0.7504	2.4147–2.8666	7	0.9941	5.17	0.9755	4.72	<i>v</i>
methane + cyclohexane	0.5380–0.7504	2.4147–2.8666	7	0.9940	12.76	1.1388	1.95	<i>v</i>
methane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	9	0.9820	11.59	1.1102	1.69	<i>w</i>
ethane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	6	0.9741	10.29	1.0848	2.63	<i>w</i>
propane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	6	0.9685	9.19	1.0655	2.71	<i>w</i>
CO ₂ + toluene	0.4951–0.5542	2.8676–2.9797	10	0.9736	4.00	1.0075	3.08	<i>x</i>
hydrogen + <i>n</i> -dodecane	0.5654–0.8617	2.1714–2.8896	8	0.9858	4.32	1.0173	3.55	<i>y</i>
CO + <i>n</i> -dodecane	0.4621–0.8617	2.1714–3.0743	9	0.9581	6.21	1.0044	5.38	<i>y</i>
CO ₂ + <i>n</i> -dodecane	0.4621–0.8617	2.1714–3.0743	9	0.9339	13.06	1.0727	2.77	<i>y</i>
hydrogen + <i>n</i> -hexadecane	0.4476–0.7814	2.3924–3.1789	10	0.9712	26.34	0.7635	6.74	<i>y</i>
CO + <i>n</i> -hexadecane	0.4476–0.7814	2.3924–3.1370	10	0.9348	7.03	0.8757	5.63	<i>y</i>
CO ₂ + <i>n</i> -hexadecane	0.4476–0.7814	2.3924–3.1456	10	0.9054	8.96	0.9914	4.66	<i>y</i>
CCl ₄ + cyclohexane	0.5380–0.7504	2.4147–2.8666	7	0.9823	19.62	0.8202	3.07	<i>v</i>

Table 5 (Continued)

system (solute + solvent)	T_{r2}	ρ_{r2}	NDP	prediction		correlation		ref
				A_D^{hh}	AAD	A_D^{ii}	AAD	
Diffusion in Liquids								
benzene + cyclohexane	0.5381–0.9441	1.7777–2.8962	12	0.9807	7.25	0.9120	5.55	<i>z,aa</i>
toluene + cyclohexane	0.5381–0.9441	1.7777–2.8962	12	0.9762	5.33	0.9256	3.17	<i>z,aa</i>
<i>m</i> -xylene + cyclohexane	0.5471–0.6013	2.7999–2.8962	4	0.9700	3.15	0.8567	2.24	<i>aa</i>
<i>p</i> -xylene + cyclohexane	0.5381–0.9441	1.7777–2.8666	8	0.9706	2.84	0.9452	1.33	<i>aa</i>
mesitylene + cyclohexane	0.5381–0.9441	1.7777–2.8962	12	0.9656	11.25	0.8654	4.88	<i>z,aa</i>
naphthalene + cyclohexane	0.5381–0.9441	1.7777–2.8962	12	0.9723	8.88	0.8907	4.80	<i>z,aa</i>
phenanthrene + cyclohexane	0.5381–0.9441	1.7777–2.8666	8	0.9465	9.10	0.8656	4.03	<i>z</i>
acetone + cyclohexane	0.5471–0.6013	2.7999–2.8962	4	0.9722	0.59	0.9665	0.08	<i>aa</i>
benzene + <i>n</i> -hexane	0.5872–1.0703	1.3481–3.0561	24	0.9727	6.32	0.9712	6.31	<i>aa,bb,cc</i>
toluene + <i>n</i> -hexane	0.5974–1.0703	1.3481–2.8637	20	0.9673	4.72	0.9672	4.72	<i>aa,bb</i>
<i>m</i> -xylene + <i>n</i> -hexane	0.5974–0.6566	2.7521–2.8637	5	0.9602	6.67	0.8994	2.79	<i>aa</i>
<i>p</i> -xylene + <i>n</i> -hexane	0.6171–1.0703	1.3481–2.8637	17	0.9608	5.56	0.9613	5.55	<i>aa,bb</i>
mesitylene + <i>n</i> -hexane	0.5974–1.0703	1.3481–2.8637	20	0.9551	5.48	0.9182	4.04	<i>aa,bb</i>
naphthalene + <i>n</i> -hexane	0.5974–1.0703	1.3481–2.8637	20	0.9628	4.65	0.9637	4.65	<i>aa,bb</i>
phenanthrene + <i>n</i> -hexane	0.6566–1.0703	1.3481–2.6705	15	0.9336	4.71	0.9141	4.79	<i>bb</i>
acetone + <i>n</i> -hexane	0.5974–0.6566	2.7521–2.8637	5	0.9627	3.23	0.9854	2.83	<i>aa</i>
carbon disulfide + <i>n</i> -hexane	0.5876–0.5876	2.8122–3.4665	10	0.9820	15.14	0.8518	2.84	<i>dd</i>
acetonitrile + <i>n</i> -hexane	0.5876–0.5876	2.8122–3.4674	7	0.9600	11.37	0.8603	3.87	<i>dd</i>
<i>n</i> -octane + <i>n</i> -heptane	0.5534–0.8828	2.2353–2.9290	4	0.9439	4.87	0.9916	2.54	<i>ee</i>
<i>n</i> -decane + <i>n</i> -heptane	0.5534–0.8828	2.2353–2.9290	5	0.9301	2.68	0.9287	2.64	<i>ee</i>
<i>n</i> -dodecane + <i>n</i> -heptane	0.5534–0.8828	2.2353–2.9437	5	0.9157	2.99	0.9122	2.98	<i>ee</i>
<i>n</i> -tetradecane + <i>n</i> -heptane	0.5534–0.8828	2.2353–2.9437	5	0.9146	7.39	0.8506	3.39	<i>ee</i>
<i>n</i> -hexadecane + <i>n</i> -heptane	0.5534–0.8828	2.1638–2.9437	8	0.8838	8.45	0.8140	3.06	<i>ee</i>
<i>n</i> -pentane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	6	0.9571	8.30	1.0425	2.94	<i>w</i>
<i>n</i> -heptane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	6	0.9439	3.79	0.9438	3.79	<i>w</i>
<i>n</i> -decane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	6	0.9221	3.59	0.9402	3.47	<i>w</i>
<i>n</i> -dodecane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	6	0.9069	2.24	0.8993	2.22	<i>w</i>
<i>n</i> -tetradecane + <i>n</i> -octane	0.5345–0.7648	2.4707–2.9945	6	0.9057	5.33	0.8591	2.50	<i>w</i>
benzene + <i>n</i> -octane	0.5331–0.5858	2.8882–2.9974	4	0.9619	13.11	1.1059	2.93	<i>ff</i>
toluene + <i>n</i> -octane	0.5331–0.5858	2.8882–2.9974	4	0.9556	9.76	1.0575	3.03	<i>ff</i>
<i>p</i> -xylene + <i>n</i> -octane	0.5331–0.5858	2.8882–2.9974	4	0.9480	13.42	1.0948	1.10	<i>ff</i>
<i>o</i> -xylene + <i>n</i> -octane	0.5331–0.5858	2.8882–2.9974	4	0.9494	7.17	1.0226	0.88	<i>ff</i>
ethylbenzene + <i>n</i> -octane	0.5331–0.5858	2.8882–2.9974	4	0.9505	3.19	0.9506	3.19	<i>ff</i>
mesitylene + <i>n</i> -octane	0.5331–0.5858	2.8882–2.9974	4	0.9415	1.75	0.9289	1.07	<i>ff</i>
<i>n</i> -octane + <i>n</i> -dodecane	0.4619–0.8599	2.1896–3.1067	9	0.9069	1.94	0.8918	0.81	<i>ee</i>
<i>n</i> -decane + <i>n</i> -dodecane	0.4619–0.8599	2.1896–3.1067	5	0.8893	5.06	0.8460	2.13	<i>ee</i>
<i>n</i> -tetradecane + <i>n</i> -dodecane	0.4619–0.8599	2.1896–3.1067	5	0.8700	17.75	0.7368	4.76	<i>ee</i>
<i>n</i> -hexadecane + <i>n</i> -dodecane	0.4919–0.8599	2.1896–3.1067	5	0.8324	18.02	0.7035	3.72	<i>ee</i>
acetone + <i>n</i> -dodecane	0.4607–0.5214	3.0389–3.1519	5	0.9234	6.44	0.8673	1.44	<i>aa</i>
benzene + <i>n</i> -dodecane	0.4607–0.5062	3.0682–3.1519	4	0.9381	10.15	0.8514	1.18	<i>aa</i>
toluene + <i>n</i> -dodecane	0.4607–0.5062	3.0682–3.1519	4	0.9301	6.52	0.8727	1.84	<i>aa</i>
<i>m</i> -xylene + <i>n</i> -dodecane	0.4607–0.5062	3.0682–3.1519	4	0.9199	8.33	0.8486	1.99	<i>aa</i>
mesitylene + <i>n</i> -dodecane	0.4607–0.5062	3.0682–3.1519	4	0.9127	13.92	0.8007	2.36	<i>aa</i>
naphthalene + <i>n</i> -dodecane	0.4607–0.5214	3.0389–3.1519	5	0.9236	9.53	0.8426	2.12	<i>aa</i>
<i>n</i> -octane + <i>n</i> -hexadecane	0.4476–0.7814	2.3962–3.1416	10	0.8734	2.15	0.8579	1.71	<i>gg</i>
<i>n</i> -decane + <i>n</i> -hexadecane	0.4476–0.7814	2.3962–3.1382	5	0.8531	4.07	0.8239	3.25	<i>gg</i>
<i>n</i> -dodecane + <i>n</i> -hexadecane	0.4476–0.7814	2.3962–3.1382	5	0.8324	4.30	0.7976	2.29	<i>gg</i>
<i>n</i> -tetradecane + <i>n</i> -hexadecane	0.4476–0.7814	2.3962–3.1382	5	0.8310	7.76	0.7703	2.74	<i>gg</i>

^a Hu and Kobayashi (1970). ^b Takahashi and Hongo (1982). ^c Imotev and Tsekhanskaya (1964). ^d Lamb et al. (1989). ^e Umezawa and Nagashima (1992). ^f Swaid and Schneider (1979). ^g Suarez et al. (1993). ^h Sassi et al. (1987). ⁱ Levelt Sengers et al. (1993). ^j Bueno et al. (1993). ^k Lai and Tan (1995). ^l Akgerman et al. (1996). ^m Catchpole and King (1994). ⁿ Debenedetti and Reid (1986). ^o Lauer et al. (1983). ^p Dahmen et al. (1990). ^q Nishiumi et al. (1996). ^r Liong et al. (1992). ^s Funazukuri et al. (1991). ^t Kopner et al. (1987). ^u Sun and Chen (1985a). ^v Chen et al. (1981). ^w Erkey and Akgerman (1989a). ^x Littel et al. (1992). ^y Matthews et al. (1987b). ^z Sun and Chen (1985b). ^{aa} Funazukuri et al. (1994). ^{bb} Sun and Chen (1985c). ^{cc} Erkey and Akgerman (1989b). ^{dd} Dymond and Woolf (1982). ^{ee} Matthews and Akgerman (1987). ^{ff} Fan et al. (1995). ^{gg} Matthews et al. (1987a). ^{hh} Values calculated with eq 48. ⁱⁱ Fitted values.

Equation 32 is not expected to provide reliable values for F_{12} at low (<0.25) and high (>1.0) molecular size ratios.

Table 3 summarizes the MD simulations and the expressions proposed by various authors for F_{12} .

Equations for the Tracer Diffusion Coefficients of Lennard–Jones and Real Fluids

As in a previous paper on the self-diffusion coefficient (Ruckenstein and Liu, 1997), we employ as the basic equation for the tracer diffusion coefficient of a solute in a real fluid the following rough Lennard–Jones (RLJ) expression:

$$D_{12}^{\infty} = A_D D_{12}^{\text{LJ}}(\rho_2^*, T^*; \sigma_{12}^{\text{LJ}}, \epsilon_{12}^{\text{LJ}}/k) \quad (35)$$

where A_D is the coupling factor treated as a constant, rather than a temperature-dependent function as in the original RHS theory. The tracer diffusion coefficient in the LJ fluid, D_{12}^{LJ} , is given by (Rice and Gray, 1965)

$$D_{12}^{\text{LJ}} = \frac{kT}{\xi_{12}^{\text{R}} + \xi_{12}^{\text{S}}} \quad (36)$$

where ξ_{12}^{R} is the friction coefficient due to repulsive interactions and ξ_{12}^{S} the friction coefficient due to the soft attractive interaction. For a hard sphere fluid, $\xi_{12}^{\text{S}} = 0$, and eq 36 reduces to eq 4.

The equation for a LJ fluid can be obtained by transforming the equation for a HS fluid in two steps: (1) introducing the attractive contribution, ξ_{12}^{S} , and (2)

replacing the molecular diameter with an effective hard sphere diameter (EHSD), which is dependent on temperature or on both temperature and density. In this way, the following equation for the self-diffusion in a LJ fluid was obtained (Ruckenstein and Liu, 1997):

$$D_{22}^{\text{LJ}} = \frac{kT}{^{8/3}\rho_2\sigma_{e22}^2(\pi m_2 kT)^{1/2} \left[\frac{g(\sigma_{e22})}{F_{22}(\rho_{e2}^*)} + \frac{0.4}{T_2^{*1.5}} \right]} \quad (37)$$

where $T_2^* = kT/\varepsilon_{22}^{\text{LJ}}$, F_{22} is given by eq 11, the radial distribution function is given by eq 33, and the reduced density, ρ_{e2}^* , is defined as The reduced EHSD, σ_{e22}^* , is

$$\rho_{e2}^* = \rho_2^* \sigma_{e22}^* = \rho_2^* \frac{\sigma_{e22}}{\sigma_{22}^{\text{LJ}}} \quad (38)$$

given by the Boltzmann expression for the repulsive Weeks–Chandler–Anderson LJ fluid (Weeks et al., 1971; Ben-Amotz and Herschbach, 1990):

$$\sigma_{e22}^* = 1.1532 \left[1 + \left(\frac{T_2^*}{0.527} \right)^{1/2} \right]^{-1/6} \quad (39)$$

The parameters in eq 39 were determined by Ben-Amotz and Herschbach (1990) by fitting the Carnahan–Starling–van der Waals equation of state to the Monte Carlo simulations for the LJ fluid.

Equation 37 provides excellent predictions for the self-diffusion in a LJ fluid (Ruckenstein and Liu, 1997). By using a similar approach, the following equation can be obtained from eq 36:

$$D_{12}^{\text{LJ}} = \frac{kT}{^{8/3}\rho_2\sigma_{e12}^2(2\pi m_{12} kT)^{1/2} \left[\frac{g(\sigma_{e12})}{F_{12}} + \frac{0.4}{T_{12}^{*1.5}} \right]} \quad (40)$$

where m_{12} is given by eq 6, $g(\sigma_{e12})$ by eq 34, F_{12} by eq 32, T_{12}^* by eq 41, and σ_{e12} by eq 42.

$$T_{12}^* = kT/\varepsilon_{12}^{\text{LJ}} \quad (41)$$

$$\sigma_{e12} = \sigma_{12}^{\text{LJ}} \sigma_{e2}^* = 1.1532 \sigma_{12}^{\text{LJ}} \left[1 + \left(\frac{T_{12}^*}{0.527} \right)^{1/2} \right]^{-1/6} \quad (42)$$

In $g(\sigma_{e12})$ and F_{12} , the molecular diameters, σ_1 and σ_2 , for a HS fluid have been replaced by the EHSDs, $\sigma_{e1} = \sigma_{11}^{\text{LJ}} \sigma_{e11}^*(T_{11}^*)$ and $\sigma_{e2} = \sigma_{22}^{\text{LJ}} \sigma_{e22}^*(T_{22}^*)$. The combining rules used in this paper for σ_{12}^{LJ} and $\varepsilon_{12}^{\text{LJ}}/k$ are

$$\sigma_{12}^{\text{LJ}} = \frac{\sigma_{11}^{\text{LJ}} + \sigma_{22}^{\text{LJ}}}{2} \quad (43)$$

and

$$\varepsilon_{12}^{\text{LJ}}/k = \sqrt{(\varepsilon_{11}^{\text{LJ}}/k)(\varepsilon_{22}^{\text{LJ}}/k)} \quad (44)$$

Consequently, the only parameter left to be determined from diffusion data is the coupling factor, A_D , introduced in eq 35. As pointed out in the last section, the expression for F_{12} , eq 32, is valid in limited ranges of molecular size and mass ratios: σ_1/σ_2 from 0.25 to 1.0, and m_1/m_2 from 1/5625 to 4.0. For some of the real systems considered in this paper the molecular size and mass ratios are outside these ranges; for this reason, a factor, which was empirically determined by fitting the

experimental data, has been introduced to make the final equation valid in wide ranges of molecular size and weight ratios. As a result, instead of eq 35, the final equation has the following form:

$$D_{12}^\infty = A_D \left(\frac{\sigma_1}{\sigma_2} \right)^{0.42} \left(\frac{m_1}{m_2} \right)^{0.06} D_{12}^{\text{LJ}} = A_D \left(\frac{V_{C1}}{V_{C2}} \right)^{0.14} \left(\frac{M_1}{M_2} \right)^{0.06} D_{12}^{\text{LJ}} \quad (45)$$

where D_{12}^{LJ} is given by eq 40 and V_C is the critical volume. For obtaining a predictive equation, the following equations (Ruckenstein and Liu, 1997) for the molecular size and energy parameters are employed:

$$\sigma_{ii}^{\text{LJ}} = 0.7889 V_{Ci}^{1/3} \quad (46)$$

$$\varepsilon_{ii}^{\text{LJ}}/k = T_{Ci}/1.2593 \quad (47)$$

where $i = 1$ or 2 and T_C is the critical temperature. In eq 46, the critical volume is expressed in cm^3/mol and σ_{ii}^{LJ} in Å.

Finally, we found that the coupling factor, A_D , in eq 45 can be correlated with the acentric factor using the following simple expression:

$$A_D = 1 + c_1 \omega_{12} + c_2 \omega_{12}^2 \quad (48)$$

where c_1 and c_2 are universal constants and the binary acentric factor, ω_{12} , is calculated from those of the pure substances using the following combining rule:

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \quad (49)$$

The combination of eqs 45–49 leads to a three-parameter corresponding-state expression for the infinitely dilute diffusion coefficients of a solute in a solvent:

$$D_{r12} = D_{r12}(T_{r12}, \rho_{r2}, \omega_{12}) \quad (50)$$

where $D_{r12} \equiv (M_2/RT_{C2})^{1/2} (D_{12}^\infty/V_{C2}^{1/3})$ is a dimensionless quantity, $T_{r12} = T/T_{C12}$ with $T_{C12} = \sqrt{T_{C1} T_{C2}}$, and $\rho_{r2} = \rho_2/\rho_{C2}$. The input data needed for the prediction are the critical temperature, critical volume, and the acentric factor for both solute and solvent.

Calculation Results and Discussion

Equation 45, combined with eqs 6,32–34,40–49, represents the working equation obtained in this paper. For testing the equation a large number of experimental data from literature have been used, namely 1443 points for 120 systems, including the diffusion coefficients in gases (157 data points for 6 systems), in supercritical fluids (793 data points for 51 systems), and in liquids (493 data points for 63 systems). The solutes and solvents involved vary from simple gases to complex heavy compounds.

The critical constants and the acentric factor for pure compounds were obtained from Reid et al. (1987) when available there, or estimated by the methods suggested in the same reference (Reid et al., 1987) when not available there. The constants for the compounds considered in this paper are listed in Table 4.

For most systems, the values of the solvent densities can be found in the same references as those for the diffusion coefficient. For carbon dioxide and ethylene, when the density data were not reported in the same

Table 6. Summary of the Calculation Results

system	NS ^a	NDP ^b	AAD	
			prediction	correlation
diffusion in gases	6	157	6.42	4.18
diffusion in SCFs	51	793	9.24	6.24
diffusion in liquids	63	493	7.74	3.72
total	120	1443	8.42	5.10

^a NS = number of systems. ^b NDP = number of data points.

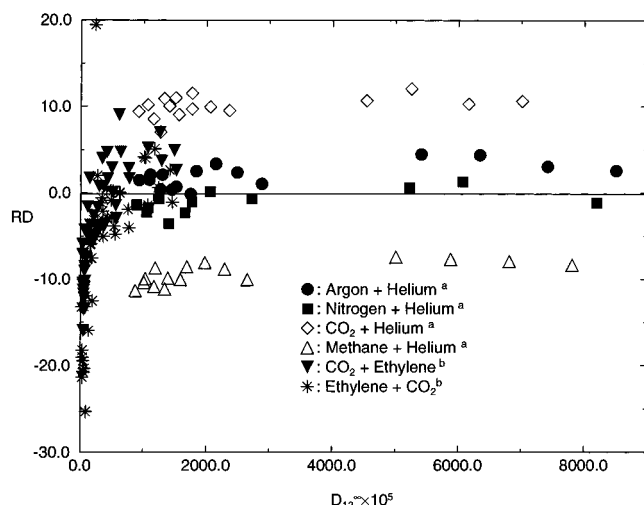


Figure 5. Relative deviations ($RD = 100(D_{12}^{cal} - D_{12}^{exp})/D_{12}^{exp}$) for the diffusion coefficients of some solutes in gases. The D_{12} 's (in cm^2/s) are the experimental values. Data sources: (a) Hu and Kobayashi (1970); (b) Takahashi and Hongo (1982).

references as the diffusion coefficients, they were estimated using the equations of state of Pitzer and Schreiber (1988) and Jahangiri et al. (1986), respectively. Another equation for carbon dioxide is also available (Span and Wagner, 1996).

The systems, data sources, and the calculated results are listed in Table 5. For comparison purposes, both the predicted (using eq 48 to estimate A_D) and correlated (taking A_D as an adjustable constant parameter for each pair) results are included in the table. For most systems, the values of the universal constants in eq 48 are $c_1 = -0.0133$ and $c_2 = -0.3662$. For the data for alkanes ($n\text{-C}_5\text{--}n\text{-C}_{14}$) + CO_2 taken from Umezawa and Nagashima (1992), different values had to be used: $c_1 = 0.5$ and $c_2 = 1.324$. The same inconsistency was noted before for the same data when a different approach for diffusion coefficient in SCF systems (Liu and Ruckenstein, 1997) was employed. It is possible that the measured diffusion coefficients involved (Umezawa and Nagashima 1992) had a systematic error of 20%–30%.

Table 6 provides a summary of the deviations for each group of systems. Tables 5 and 6 show that, for all systems, the one-parameter equation, in which A_D is determined from the diffusion data, provides an accurate correlation with deviations within the experimental uncertainties: the grand AAD for all the systems is only 5.1%. Higher deviations were observed for SCF systems, since the experimental uncertainties are higher for those cases (Liong et al., 1991). For most systems, the predictions based on eq 48 for A_D are excellent with an AAD comparable to the experimental uncertainties. The grand AAD for all systems is only 8.42%.

As is well-known, the diffusion coefficient varies considerably from gaseous to liquid systems, typically from 10^{-1} to $10^{-5} \text{ cm}^2/\text{s}$ (see Figures 5–7). Nevertheless,

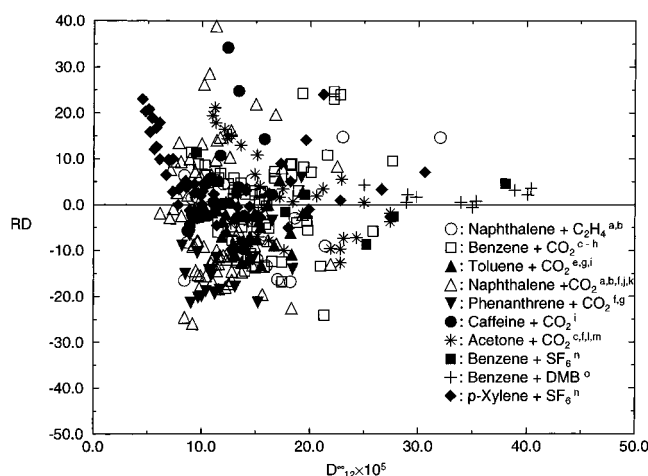


Figure 6. Relative deviations ($RD = 100(D_{12}^{cal} - D_{12}^{exp})/D_{12}^{exp}$) for the diffusion coefficients of some solutes in supercritical fluids. The D_{12} 's (in cm^2/s) are the experimental values. Data sources: (a) Imotev and Tsehanskaya (1964); (b) Lamb et al. (1989); (c) Umezawa and Nagashima (1992); (d) Swaid and Schneider (1979); (e) Suarez et al. (1993); (f) Sassi et al. (1987); (g) Levelt Sengers et al. (1993); (h) Bueno et al. (1993); (i) Lai and Tan (1995); (j) Akgerman et al. (1996); (k) Lauer et al. (1983); (l) Dahmen et al. (1990); (m) Nishiumi et al. (1996); (n) Kopner et al. (1987); (o) Sun and Chen (1985a).

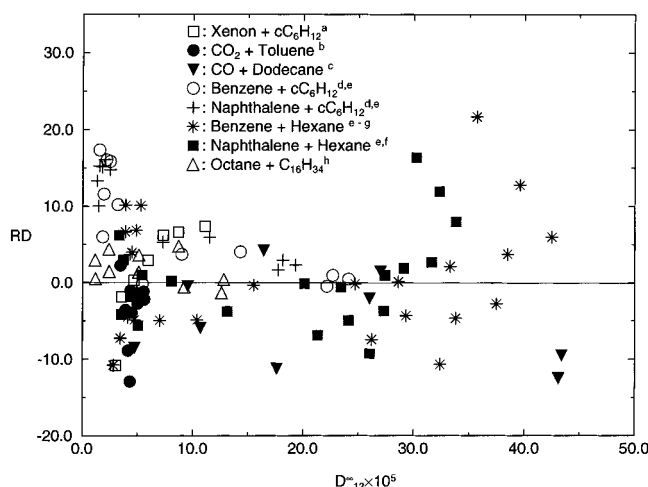


Figure 7. Relative deviations ($RD = 100(D_{12}^{cal} - D_{12}^{exp})/D_{12}^{exp}$) for the diffusion coefficients of some solutes in liquids. The D_{12} 's (in cm^2/s) are the experimental values. Data sources: (a) Chen et al. (1981); (b) Littel et al. (1992); (c) Matthews et al. (1987b); (d) Sun and Chen (1985b); (e) Funazukuri et al. (1994); (f) Sun and Chen (1985c); (g) Erkey and Akgerman (1989b); (h) Matthews et al. (1987a).

eq 45 can represent the diffusion behavior over a wide range of densities, ρ_{r2} from 0.036 to 3.15. Figures 5–7 show that the deviations for diffusion in gases, supercritical fluids, and liquids are small.

As noted in our previous paper (Ruckenstein and Liu, 1997), the self-diffusion coefficients are very sensitive to the molecular diameter, σ_{ii}^{LJ} ($i = 1, 2$). For the binary systems considered here, it was found that the tracer diffusion coefficients are more sensitive to the molecular diameter of the solvent, σ_{22}^{LJ} , than to that of the solute, σ_{11}^{LJ} . Nevertheless, the sensitivity to σ_{22}^{LJ} in the binary diffusion is lower than in the self-diffusion. Consequently, both the diameters of the solute and solvent can be estimated using eq 46. More accurate values for the critical volumes will be useful (Eaton and Akgerman, 1997), but as shown by Table 5, the sensitivity of

our equation to the value of the critical volume is not as high as that observed by Eaton and Akgerman (1997).

To avoid using the critical volume, some authors correlated the molecular diameter with the critical pressure and temperature (Hirschfelder et al., 1964; Tee et al., 1966). For this reason, we have also used the expression $\sigma_{ij}^{LJ} = 0.5058(RT_C/P_C)^{1/3}$ (Ruckenstein and Liu, 1997) in our prediction, but the deviations were higher.

Finally, as in the case of self-diffusion coefficients (Ruckenstein and Liu, 1997), the established equation leads to higher deviations (20%–30%) for hydrogen-bonded solvents, such as alcohols and water.

Conclusions

A new expression was obtained for the tracer diffusion coefficient in hard sphere fluids on the basis of the molecular dynamics simulations of Herman and Alder (1972) and Alder et al. (1974). The expression is extended to a Lennard–Jones fluid by replacing the molecular sizes with the effective hard sphere diameters and by introducing the attractive contribution. Finally, the equation is extended to real fluids by introducing a coupling factor which accounts for the nonsphericity of the molecules. A large number of experimental data were employed to test the equation. It was shown that the obtained equation can be used with high accuracy to predict the tracer diffusion coefficients of various solutes in gases, supercritical fluids, and liquids.

The input data needed for prediction are the critical temperature, critical volume, and the acentric factor for pure compounds. Simple combining rules were used for the binary interaction parameters, σ_{12}^{LJ} and ϵ_{12}^{LJ}/k , and the only parameter which was determined from tracer diffusion data was the coupling factor A_D . This factor could be expressed in terms of the acentric factor ω_{12} . For those systems for which reliable critical constants, especially the critical volume, are available, the prediction accuracy was comparable to the experimental one. The results obtained show that a three-parameter (T_C, V_C, ω) expression is applicable to all systems with somewhat higher deviations for hydrogen-bonded solvents.

Nomenclature

a = parameter given by eq 27c
 a_0, a_1, a_2 = parameters in eqs 22–25
 A_D = translational–rotational coupling factor
 AAD = absolute average deviation, $AAD = (100/NDP) \sum_{i=1}^{NDP} |(D_{12i}^{cal} - D_{12i}^{exp})/D_{12i}^{exp}|$
 b_i = constants in eq 32 given in Table 2
 b_{12} = parameter given by eq 27b
 c_1, c_2 = constants in eq 48 (for most systems, $c_1 = -0.0133$ and $c_2 = -0.3662$; for n -alkanes + CO_2 , $c_1 = 0.5$ and $c_2 = 1.324$)
 $C4:0$ = butyric acid
 $C8:0$ = caprylic acid
 $C10:0$ = capric acid
 $C14:0$ = myristic acid
 $C16:0$ = palmitic acid
 $C18:0$ = stearic acid
 $C22:0$ = behenic acid
 $C18:2$ = linoleic acid
 $C20:5$ = eicosapentaenoic acid
 $C22:6$ = docosahexaenoic acid
 C_2H_2 = ethylene
 $C_{16}H_{34}$ = n -hexadecane
 CCl_4 = carbon tetrachloride
 $CClF_3$ = chlorotrifluoromethane
 CO = carbon monoxide

CO_2 = carbon dioxide
 D = diffusion coefficient, cm^2/s
 DMB = 2,3-dimethylbutane
 D_{12}^∞ = tracer diffusion coefficient of solute 1 in solvent 2, cm^2/s
 $EHSD$ = effective hard sphere diameter
 F_{12}, F_{22} = functions defined by eqs 4 and 9, respectively
 $g(\sigma_{22}), g(\sigma_{12})$ = radial distribution function at contact for pure solvent and infinitely dilute binary system, respectively
 G_i = functions defined in Table 2
 h_{12} = function in eq 24
 HS = hard sphere
 k = Boltzmann constant, 1.38048×10^{-23} , J/K
 LJ = Lennard–Jones
 I_{12} = binary interaction parameter in eq 2
 m = mass of a molecule, kg
 M = molecular weight, g/mol
 MD = molecular dynamics
 N_a = Avogadro number, 6.023×10^{23} , mol^{-1}
 NDP = number of data points
 NS = number of systems
 P = pressure, bar
 R = gas constant
 RLJ = rough Lennard–Jones
 RD = relative deviation, $RD = 100(D_{12}^{cal} - D_{12}^{exp})/D_{12}^{exp}$
 RHS = rough hard sphere
 SF_6 = sulfur hexafluoride
 T = temperature, K
 $T_r = T/T_C$
 V = molar volume, cm^3/mol
 V_0 = closed-packed molar volume, $N_a \sigma_{22}^3 / \sqrt{2}$, cm^3/mol

Greek Letters

α = parameter given by eq 27a
 $\eta_2 = \pi \rho_2 \sigma_{22}^3 / 6$ for HS fluid, $\pi \rho_2 \sigma_{e22}^2 / 6$ for LJ and real fluids
 Δ = function defined by eq 31
 ϵ^{LJ}/k = Lennard–Jones energy parameter, K
 $\chi = \rho_2^{*0.01}$
 γ, γ_B = quantities introduced in eq 15
 μ_2 = viscosity of the HS solvent
 μ_0 = viscosity of gas at very low density
 ω = acentric factor
 ρ_2 = number density of solvent, N_a/V_2
 $\rho_r = \rho/\rho_c$
 σ^{LJ} = Lennard–Jones molecular diameter parameter, cm
 ξ = friction coefficient

Subscripts

1 or 11 = solute
 2 or 22 = solvent
 12 = binary property
 C = critical constant
 e = effective hard sphere diameter
 r = reduced quantity

Superscripts

$*$ = reduced property
 ∞ = infinite dilution for solute
 0 = solvent
 E = Enskog theory
 H = hydrodynamic contribution
 HS = hard sphere fluid
 LJ = Lennard–Jones fluid
 R = repulsive contribution
 S = soft attractive contribution

Literature Cited

Alder, B. J.; Gass, D. M.; Wainwright, T. E. Studies in Molecular Dynamics. VIII. The Transport Coefficients for a Hard-Sphere Fluid. *J. Chem. Phys.* **1970**, *53*, 3813–3826.

- Alder, B. J.; Alley, W. E.; Dymond, J. H. Studies in Molecular Dynamics. XIV. Mass and Size Dependence of the Binary Diffusion Coefficient. *J. Chem. Phys.* **1974**, *61*, 1415–1420.
- Akgerman, A.; Erkey, C.; Orejuela, M. Limiting Diffusion Coefficients of Heavy Molecular Weight Organic Contaminants in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1996**, *35*, 911–917.
- Ben-Amotz, D.; Herschbach, D. Estimation of Effective Diameters for Molecular Fluids. *J. Phys. Chem.* **1990**, *94*, 1038–1047.
- Bertucci, S. J.; Flygare, W. H. Rough Hard Sphere Treatment of Mutual Diffusion in Binary Liquid Mixtures. *J. Chem. Phys.* **1975**, *63*, 1–9.
- Bueno, J. L.; Suarez, J. J.; Dizy, J.; Medina, I. Infinite Dilution Diffusion Coefficients: Benzene-Derivatives as Solutes in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1993**, *38*, 344–349.
- Carnahan, N. F.; Starling, K. E. Equation of State for Nonattractive Rigid Spheres. *J. Chem. Phys.* **1969**, *51*, 635–636.
- Catchpole, O. J.; King, M. B. Measurement and Correlation of Binary Diffusion Coefficients in Near Critical Fluids. *Ind. Eng. Chem. Res.* **1994**, *33*, 1828–1837.
- Chandler, D. Rough Hard Sphere Theory of the Self-Diffusion Constant for Molecular Liquids. *J. Chem. Phys.* **1975**, *62*, 1358–1365.
- Chapman, S.; Cowling, T. G. *The Mathematical Theory of Non Uniform Gases*; Cambridge University Press: Cambridge, 1970.
- Chen, S.-H. A Rough-Hard-Sphere Theory for Diffusion in Supercritical Carbon Dioxide. *Chem. Eng. Sci.* **1983**, *38*, 655–660.
- Chen, S.-H.; Davis, H. T.; Evans, D. F. Tracer Diffusion in Polyatomic Liquids. *J. Chem. Phys.* **1981**, *75*, 1422–1426.
- Dahmen, N.; Kordikowski, A.; Schneider, G. M. Determination of Binary Diffusion Coefficients of Organic Compounds in Supercritical Carbon Dioxide by Supercritical Fluid Chromatography (SFC). *J. Chromatogr.* **1990**, *505*, 169–176.
- Darken, L. S. Diffusion, Mobility and Their Interrelation through Free Energy in Binary Metallic Systems. *Am. Inst. Min. Metall. Pet. Eng.* **1948**, *175*, 184–190.
- Debenedetti, P. G.; Reid, R. C. Diffusion and Mass Transfer in Supercritical Fluids. *AIChE J.* **1986**, *32*, 2034–2046.
- Dymond, J. H. Hard-Sphere Theories of Transport Properties. *Chem. Soc. Rev.* **1985**, *14*, 317–356.
- Dymond, J. H.; Woolf, L. A. Tracer Diffusion of Organic Solutes in n-Hexane at Pressures up to 400 MPa. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 991–1000.
- Easteal, A. J.; Woolf, L. A. Tracer Diffusion in Hard Sphere Liquids from Molecular Dynamics Simulations. *Chem. Phys. Lett.* **1990**, *167*, 329–333.
- Easteal, A. J.; Woolf, L. A.; Jolly, D. L. Self-Diffusion in a Dense Hard-Sphere Fluid: A Molecular Dynamics Simulation. *Physica* **1983**, *121A*, 286–292.
- Easteal, A. J.; Woolf, L. A.; Jolly, D. L. On the Number Dependence of Hard-Sphere Diffusion Coefficients from Molecular Dynamics Simulation. *Physica* **1984**, *127A*, 344–346.
- Eaton, A. P.; Akgerman, A. Infinite-Dilution Diffusion Coefficients in Supercritical Fluids. *Ind. Eng. Chem. Res.* **1997**, *36*, 923–931.
- Erkey, C.; Akgerman, A. Translational-Rotational Coupling Parameters for Mutual Diffusion in n-Octane. *AIChE J.* **1989a**, *35*, 443–448.
- Erkey, C.; Akgerman, A. Translational Rotational Coupling Parameters for Mutual Diffusion in Normal Alkanes. *AIChE J.* **1989b**, *35*, 1907–1911.
- Erkey, C.; Gadalla, H.; Akgerman, A. Application of Rough Hard Sphere Theory to Diffusion in Supercritical Fluids. *J. Supercrit. Fluids* **1990**, *3*, 180–185.
- Erpenbeck, J. J.; Wood, W. W. Self-Diffusion Coefficient for the Hard-Sphere Fluid. *Phys. Rev. A* **1991**, *43*, 4254–4261.
- Fan, Y.; Qian, R.; Shi, M.; Shi, J. Infinite Dilution Diffusion Coefficients of Several Aromatic Hydrocarbons in Octane and 2,2,4-Trimethylpentane. *J. Chem. Eng. Data* **1995**, *40*, 1053–1055.
- Funazukuri, T.; Hachisu, S.; Wakao, N. Measurements of Binary Diffusion Coefficients of C₁₆–C₂₄ Unsaturated Fatty Acid Methyl Esters in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1991**, *30*, 1323–1329.
- Funazukuri, T.; Nashimoto, N.; Wakao, N. Binary Diffusion Coefficients of Organic Compounds in Hexane, Dodecane, and Cyclohexane at 303.2–333.2 K and 16.0 MPa. *J. Chem. Eng. Data* **1994**, *39*, 911–915.
- Herman, P. T.; Alder, B. J. Studies in Molecular Dynamics. XI. Correlation Functions of a Hard-Sphere Test Particle. *J. Chem. Phys.* **1972**, *56*, 987–991.
- Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1964.
- Hu, A. T.-C.; Kobayashi, R. Measurements of Gaseous Diffusion Coefficients for Dilute and Moderate Dense Gases by Perturbation Chromatography. *J. Chem. Eng. Data* **1970**, *15*, 328–335.
- Iomtev, M. B.; Tsekhanskaya, Yu V. Diffusion of Naphthalene in Compressed Ethylene and Carbon Dioxide. *Russ. J. Phys. Chem.* **1964**, *38*, 485–491.
- Jahangri, M.; Jacobsen, R. T.; Stewart, R. B.; McCarty, R. D. Thermodynamic Properties of Ethylene from the Freezing Line to 450 K at Pressures to 260 MPa. *J. Phys. Chem. Ref. Data* **1986**, *15*, 593–650.
- Kopner, A.; Hamm, A.; Ellert, J.; Feist, R.; Schneider, G. M. Determination of Binary Diffusion Coefficients in Supercritical Chlorotrifluoromethane and Sulphurhexafluoride with Supercritical Fluid Chromatography (SFC). *Chem. Eng. Sci.* **1987**, *42*, 2213–2218.
- Lai, C.-C.; Tan, C.-S. Measurement of Molecular Diffusion Coefficients in Supercritical Carbon Dioxide Using a Coated Capillary Column. *Ind. Eng. Chem. Res.* **1995**, *34*, 674–680.
- Lamb, D. M.; Adamy, S. T.; Woo, K. W.; Jonas, J. Transport and Relaxation of Naphthalene in Supercritical Fluids. *J. Phys. Chem.* **1989**, *93*, 5002–5005.
- Lauer, H. H.; McManigill, D.; Board, R. D. Mobile-Phase Transport Properties of Liquefied Gases in Near-Critical and Supercritical Fluid Chromatography. *Anal. Chem.* **1983**, *55*, 1370–1375.
- Levelt Sengers, J. M. H.; Deiters, U. K.; Klask, U.; Swidersky, P.; Schneider, G. M. Application of the Taylor Dispersion Method in Supercritical Fluids. *Int. J. Thermophys.* **1993**, *14*, 893–922.
- Liong, K. K.; Wells, P. A.; Foster, N. R. Diffusion in Supercritical Fluids. *J. Supercrit. Fluids* **1991**, *4*, 91–108.
- Liong, K. K.; Wells, P. A.; Foster, N. R. Diffusion of Fatty Acid Esters in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1992**, *31*, 390–397.
- Littel, R. J.; Versteeg, G. F.; van Swaaij, W. P. M. Diffusivity Measurements in Some Organic Solutes by a Gas-Liquid Diaphragm Cell. *J. Chem. Eng. Data* **1992**, *37*, 42–45.
- Liu, H.; Ruckenstein, E. Predicting the Diffusion Coefficients in Supercritical Fluids. *Ind. Eng. Chem. Res.* **1997**, *36*, 888–895.
- Liu, H.; Silva, C. M.; Macedo, E. A. New Equations for Tracer Diffusion Coefficients of Solute in Supercritical and Liquid Solvents Based on the Lennard–Jones Fluid Model. *Ind. Eng. Chem. Res.* **1997**, *36*, 246–252.
- Mansoori, G. A.; Carnahan, N. F.; Starling, K. E.; Leland, T. W., Jr. Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres. *J. Chem. Phys.* **1971**, *54*, 1523–1525.
- Matthews, M. A.; Akgerman, A. Diffusion Coefficients for Binary Alkane Mixtures to 573 K and 3.5 MPa. *AIChE J.* **1987**, *33*, 881–885.
- Matthews, M. A.; Rodden, J. B.; Akgerman, A. High-Temperature Diffusion, Viscosity, and Density Measurements in n-Hexadecane. *J. Chem. Eng. Data* **1987a**, *32*, 317–319.
- Matthews, M. A.; Rodden, J. B.; Akgerman, A. High-Temperature Diffusion of Hydrogen, Carbon Monoxide, and Carbon Dioxide in Liquid n-Heptane, n-Dodecane, and n-Hexadecane. *J. Chem. Eng. Data* **1987b**, *32*, 319–322.
- Nishiumi, H.; Fujita, M.; Agou, K. Diffusion of Acetone in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1996**, *117*, 356–363.
- Pertler, M.; Blass, E.; Stevens, G. W. Fickian Diffusion in Binary Mixtures That Form Two Liquid Phases. *AIChE J.* **1996**, *42*, 910–920.
- Pitzer, K. S.; Schreiber, D. R. Improving Equation-of-State Accuracy in the Critical Region; Equations for Carbon Dioxide and Neopentane as Examples. *Fluid Phase Equilib.* **1988**, *41*, 1–17.
- Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill Book Company: New York, 1987.
- Rice, S. A.; Gray, P. *The Statistical Mechanics of Simple Liquids*; Interscience Publishers: New York, 1965.
- Ruckenstein, E.; Liu, H. Self-Diffusion in Gases and Liquids. *Ind. Eng. Chem. Res.* **1997**, *36*, 3927–3936.
- Salim, P. H.; Trebble, M. A. Modified Interacting-Sphere Model for Self-Diffusion and Infinite-Dilution Mutual-Diffusivity of n-Alkanes. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 245–250.

- Sassiat, P. R.; Mourier, P.; Caude, M. H.; Rosset, R. Measurement of Diffusion Coefficients in Supercritical Carbon Dioxide and Correlation with the Equation of Wilke and Chang. *Anal. Chem.* **1987**, *59*, 1164–1170.
- Span, R.; Wagner, W. A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509–1596.
- Speedy, R. J. Diffusion in the Hard Sphere Fluid. *Mol. Phys.* **1987**, *62*, 509–518.
- Suarez, J. J.; Bueno, J. L.; Medina, I. Determination of Binary Diffusion Coefficients of Benzene and Derivatives in Supercritical Carbon Dioxide. *Chem. Eng. Sci.* **1993**, *48*, 2419–2427.
- Sun, C. K. J.; Chen, S. H. Diffusion of Benzene, Toluene, Naphthalene, and Phenanthrene in Supercritical Dense 2,3-Dimethylbutane. *AIChE J.* **1985a**, *31*, 1904–1910.
- Sun, C. K. J.; Chen, S. H. Tracer Diffusion of Aromatic Hydrocarbons in Liquid Cyclohexane up to its Critical Temperature. *AIChE J.* **1985b**, *31*, 1510–1515.
- Sun, C. K. J.; Chen, S. H. Tracer Diffusion of Aromatic Hydrocarbons in n-Hexane up to the Supercritical Region. *Chem. Eng. Sci.* **1985c**, *40*, 2217–2224.
- Sun, C. K. J.; Chen, S. H. Tracer Diffusion in Dense Ethanol: A Generalized Correlation for Nonpolar and Hydrogen-Bonded Solvents. *AIChE J.* **1986**, *32*, 1367–1371.
- Sung, W.; Stell, G. Theory of Transport in Dilute Solutions, Suspensions, and Pure Fluids: I. Translational Diffusion. *J. Chem. Phys.* **1984**, *80*, 3350–3366.
- Swaid, I.; Schneider, G. M. Determination of Binary Diffusion Coefficients of Benzene and Some Alkylbenzenes in Supercritical CO₂ Between 308 and 328 K in the Pressure Range 80 to 160 bar with Supercritical Fluid Chromatography (SFC). *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 969–977.
- Takahashi, S.; Hongo, M. Diffusion Coefficients of Gases at High Pressures in the CO₂–C₂H₄ System. *J. Chem. Eng. Jpn.* **1982**, *15*, 57–59.
- Tee, L. S.; Gotoh, S.; Stewart, W. E. Molecular Parameters for Normal Fluids. The Lennard–Jones 12-6 Potential. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 356–363.
- Umezawa, S.; Nagashima, A. Measurement of the Diffusion Coefficients of Acetone, Benzene, and Alkane in Supercritical CO₂ by the Taylor Dispersion Method. *J. Supercrit. Fluid* **1992**, *5*, 242–250.
- Vignes, A. Diffusion in Binary Solutions—Variation of Diffusion Coefficient with Composition. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 189–199.
- Weeks, J. D.; Chandler, D.; Andersen, H. C. Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids. *J. Chem. Phys.* **1971**, *54*, 5237–5247.
- Wilke, C. R.; Chang, P. R. Correlations of Diffusion Coefficients in Dilute Solutions. *AIChE J.* **1955**, *1*, 264–269.
- Woodcock, L. V. Diffusivity of the Hard-Sphere Model in the Region of Fluid Metastability. *Ann. N. Y. Acad. Sci.* **1981a**, *371*, 274.
- Woodcock, L. V.; Angell, C. A. *Phys. Rev. Lett.* **1981b**, *47*, 1129–1133.

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