NOTATION

c_A = concentration of solute A in fluid phase, g solute/cm^3 fluid
D = diameter of resin particles, cm
q_A = concentration of solute A in resin phase
Q = fluid flow rate at bed inlet (Q_i) or outlet (Q_e), cm^3/min
S = bed cross-sectional area, cm^2
t = time, min
T = breakthrough time of sharp concentration front, min
V = bed volume, cm^3
x_A = concentration of solute A in fluid phase, g solute/g fluid
y_A = concentration of solute A in resin phase, g solute/g resin phase
Z^0 = initial bed length
ΔZ = length of zone between the bed inlet and the concentration discontinuity, cm

Greek Letters

ϵ = bed void fraction, dimensionless
ρ = density of fluid phase, g/cm^3
ρ_r = density of resin phase, g/cm^3

Subscripts

0 = refers to conditions in the sorption zone between the concentration discontinuity and the outlet of the bed
N = refers to conditions in the sorption zone between the inlet of the bed and the concentration discontinuity

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Reduced State Correlations for the Self-Diffusivity of Dense Fluids

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In a recent article in this journal, correlations for reduced friction coefficients were presented in terms of the reduced density $\rho^* = N\sigma^3/V$ and reduced temperature $T^* = kT/\epsilon$, where σ and ϵ are the collision diameter and well depth respectively for the Lennard-Jones (12, 6) potential (Ramanan and Hamrin, 1972). These correlations were subsequently applied to experimental self-diffusivity data for several dense gases. A degree of success led Ramanan and Hamrin to conclude that "all the information necessary is now available to test theoretical equations for viscosity and thermal conductivity and to compare the results with the numerous experimental values available in the literature."

The purpose of this note is to elaborate on the development of these correlations and to discuss some apparent deficiencies in this approach. Since it is shown that the friction coefficient expressions are based on incorrect assumptions and that inaccurate distribution functions have been used in the calculation of these coefficients, the above conclusion seems unwarranted.

THEORY

In the transport theory proposed by Rice and Allnatt (1961), the pair potential is assumed to consist of a rigid core repulsion superimposed on an arbitrary soft interaction, usually the Lennard-Jones (12, 6) model:

$$\begin{aligned} \phi(r) &= \infty & r < \sigma \\ \phi(r) &= 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & r > \sigma \end{aligned} \qquad (1)$$

The friction constant, defined by the Stokes-Einstein equation, can then be separated into hard-core and soft contributions

$$\zeta = \zeta^H + \zeta^S = kT/D \qquad (2)$$

Since the hard-core friction coefficient results from rigid sphere collisions, it can be calculated from the Enskog approach (Longuet-Higgins and Pople, 1956)

$$\zeta^H = \frac{8\rho\sigma^2}{3V}(\pi mkT)^{1/2}\, g(\sigma) \qquad (3)$$

where $g(\sigma)$ is the contact radial distribution function or collision probability. The soft friction coefficient arising from weak attractive interactions in the range $r > \sigma$ is estimated from the linear trajectory approximation (Helfand, 1961)

$$\zeta^S = \frac{8\rho\sigma^2}{3V}(\pi mkt)^{1/2}\left[\frac{\epsilon}{kT}\int_0^\infty F(r)\,\{g(r) - 1\}\right] \qquad (4)$$

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The actual form of the interaction term $F(r)$ depends on the model assumed to describe molecular forces for $r > \sigma$. For the Lennard-Jones (12, 6) potential,

$$F(r) = 22 \sum_{i=1}^{6} (2i-1)^{-1} r^{(2i-12)} - 10 \sum_{j=1}^{3} (2j-1)^{-1} r^{(2j-6)} + \ln\left(\frac{r+1}{r-1}\right) (5r^{-5} - 11r^{-11}) \qquad (5)$$

It is important to note that the soft friction coefficient can be calculated in this way only if there are no large momentum exchanges between molecules (Mazo, 1967). The crux of the Rice-Allnatt theory is the assumption that such large exchanges can be treated as rigid-core repulsions and independent of the soft interactions.

The use of reduced friction coefficients was initiated by Palyvos and Davis (1967) who defined

$$\zeta_r = \zeta/\zeta^* = \zeta^H/\zeta^* + \zeta^S/\zeta^* = \zeta^H{}_r + \zeta^S{}_r$$

where

$$\zeta^* = \frac{8\rho\sigma^2}{3V} (\pi m k T)^{1/2} \qquad (6)$$

Therefore, it follows that

$$\zeta^H{}_r = g(\sigma) \qquad (7)$$

and

$$\zeta^S{}_r = f\,[g(r), T^*] \qquad (8)$$

CALCULATION OF THE FRICTION COEFFICIENTS

It can be seen in Equations (3) and (4) that the reduced friction coefficients can be calculated given the radial distribution function for the hard-core modified Lennard-Jones (12, 6) potential as a function of ρ^* and T^*. A theoretical solution for $g(r)$ for this pair potential was developed by Kirkwood, Lewinson and Alder (1952) and tabulated for a wide range of reduced temperature and reduced density. "Experimental" values of $g(r)$ have been obtained by the Monte Carlo technique at six reduced densities at each of two reduced temperatures Collings et al. (1971). These states correspond to the liquid region.

Since $\zeta^H{}_r = g(\sigma)$, the value of the radial distribution function at $r = \sigma$, correlations such as Figure 1 can be compiled directly from the theoretical expansion for $g(r)$ (Kirkwood et al. (1952). Also shown in Figure 1 are the Monte Carlo values for the reduced hard-core friction coefficient (Collings et al., 1971).

Using the theoretical $g(r)$, the integral in Equation (4) was carried out numerically by Palyvos and Davis who tabulated $\zeta^S{}_r$ for a reciprocal reduced temperature range of 0.1 to 1.5 at reduced densities of 0.443, 0.674, and 0.818. These calculations were repeated by Collings and Woolf (1971) who obtained differences of up to 8% in the high temperature region, but agreement to better than 2% in the liquid region. The results of Collings and Woolf for $\zeta^S{}_r$ using the theoretical $g(r)$ (Kirkwood et al., 1952) are shown in Figure 2, along with results based on the Monte Carlo $g(r)$ (Collings et al., 1971). The zero density values of $\zeta^S{}_r$ in Figure 2 were calculated using the zero density limit of the virial expansion for the radial distribution function

$$g(r) = \exp\,[-\phi(r)/kT] \qquad (9)$$

DISCUSSION

As mentioned earlier, the hard-core modification of the Lennard-Jones (12, 6) potential is a necessary adjunct of the Rice-Allnatt theory. However, modeling the repulsive forces in this fashion changes the values of the molecular parameters which are estimated from experimental pVT data. Ramanan and Hamrin (1972) have apparently adopted the procedure of Kirkwood et al. (1952), Palyvos and Davis (1967), and Rice and Gray (1965), and used LJ parameters. In Table 1, their values are compared with modified LJ (12, 6) parameters for the noble gases and are seen to be significantly different.

In Figure 1, we note that for a range of reduced temperature and density which corresponds to the liquid or dense gas range, $\zeta^H{}_r$ or $g(\sigma)$ is actually less than 1. This is an entirely unphysical result. If the radial distribution function is expanded in powers of density, numerical evaluations of the second term $g_1(r)$, which has units of reciprocal density, show that it is always positive for values of r just larger than σ (Henderson, 1965). Therefore, $g(\sigma)$ must always be greater than 1 for this potential. We also see that the theoretical $\zeta^H{}_r$, as a consequence of using the theoretical function of Kirkwood et al. (1952), is substantially lower than the corresponding Monte Carlo result which we can presume to be correct. The dashed curves in Figure 1 would presumably be more reliable estimates of $\zeta^H{}_r$ in the low density region.

A second, unphysical result is evident in Figure 2. In the zero density limit, ζ^S should reduce to 0 and ζ to ζ^H. This would seem to be an essential feature of any realistic dense fluid theory (McLaughlin, 1964). Equation (9) is rigorous in the zero density limit and the values of $\zeta^S{}_r$ at

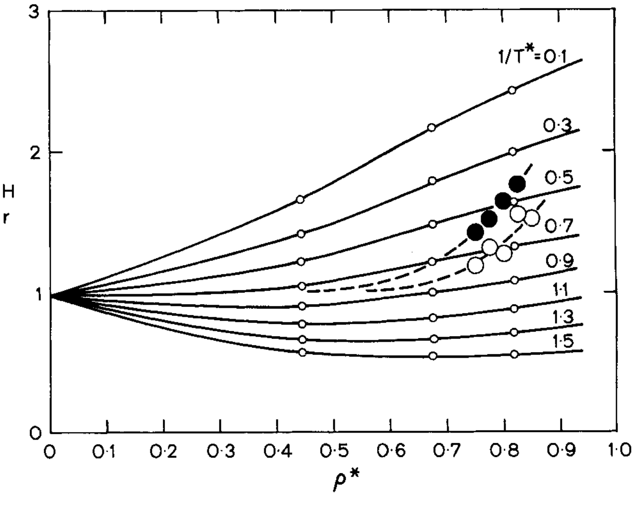

Fig. 1. The reduced, hard-core friction coefficient: estimated from theoretical $g(\sigma)$ (Kirkwood et al., 1952). —○— Monte Carlo results: ○, $1/T^* = 1.25$, ●, $1/T^* = 1.0$.

TABLE 1. VALUES OF POTENTIAL PARAMETERS

Substance	LJ (Ramanan and Hamrin) σ, A°	LJ (Ramanan and Hamrin) ϵ/k, °K	Modified LJ (Collings et al.) σ, A°	Modified LJ (Collings et al.) ϵ/k, °K
Ar	3.300	137.2	3.372	127
Kr	3.377	166.0	3.624	182
Xe	3.683	265.0	3.905	235

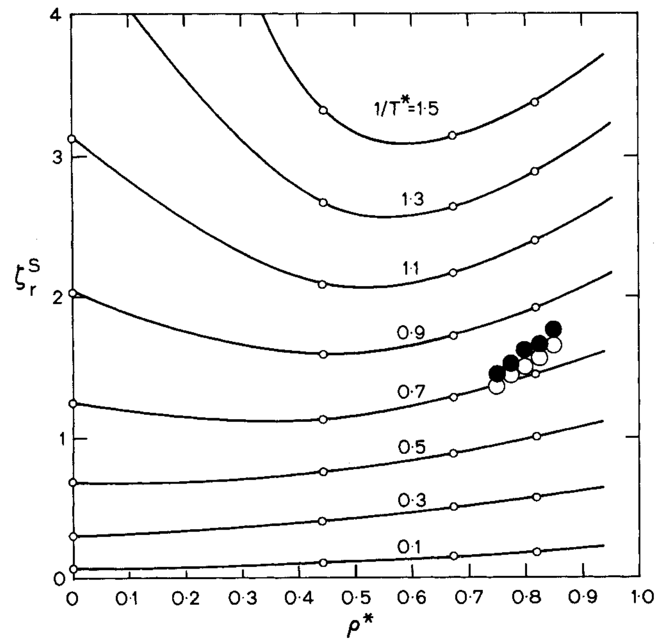

Fig. 2. The reduced, soft friction coefficient: estimated from theoretical $g(r)$ (Kirkwood et al., 1952). —○— Monte Carlo results: ○, $1/T^* = 1.0$, ●, $1/T^* = 1.25$.

$\rho^* = 0$ in Figure 2 do not seem inconsistent with values calculated from the Kirkwood expansion at higher densities. Presumably, this unreal behavior prompted Ramanan and Hamrin (1972) to ignore the lower density results from Equation (4) with the theoretical $g(r)$. They assumed that the theory was correct for argon in the low density limit and backed out values of $\zeta^S{}_r$ from experimental diffusion data setting $\zeta^H{}_r = 1.0$ (Ramanan and Hamrin, 1972). They then extrapolated the theoretical curves from $\rho^* = 0.443$ down to $\rho^* = 0$. Therefore, the reasonable agreement with data for other gas diffusivities they found in the low density region (Ramanan and Hamrin, 1972) is merely a form of the principle of corresponding states which is already known to be adequate for low density gases of simple structure. In this case, it is applied with incorrect potential parameters in an inadequate theory of transport. In their figure 4, systematic departure from the proposed correlation occurs at the higher densities corresponding to the liquid range (Ramanan and Hamrin). The lack of success of this theory in predicting liquid self-diffusivities has been noted previously (Collings and Woolf, 1971). We again see that there is a significant difference between the values of $\zeta^S{}_r$ calculated from the Monte Carlo and theoretical $g(r)$'s at high densities.

Finally, it can be pointed out that there is now considerable evidence which suggests that the Rice-Allnatt theory, at least in its application to self-diffusivity, is based on incorrect assumptions (Collings et al., 1971; Fisher and Watts, 1972). Specifically, the assumptions that ζ^S is more significant than ζ^H in dense fluids (Collings et al.) and of the existence of a plateau in the friction constant integral (Fisher and Watts) have been shown to be wrong.

Under the circumstances, a test of the equations for viscosity and thermal conductivity using the proposed friction constant correlation is not likely to be profitable.

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NOTATION

D = self-diffusivity
f = function of – – –
$F(r)$ = interaction term in the linear trajectory approximation
$g(r)$ = radial distribution function
$g(\sigma)$ = contact radial distribution function
k = Boltzmann constant
m = mass per molecule
M = molecular weight
N = Avogadro's number
r = intermolecular separation
t = time
T = absolute temperature
T^* = reduced temperature kT/ϵ
V = molecular volume

Greek Letters

ϵ = potential well depth for the LJ or modified LJ models
σ = value of r for which $\phi(r) = 0$
ϕ = intermolecular potential energy
ζ = friction coefficient
ζ^H = hard-core friction coefficient
ζ^S = soft friction coefficient
ζ_r = reduced friction coefficient
$\zeta^H{}_r$ = reduced hard-core friction coefficient
$\zeta^S{}_r$ = reduced soft friction coefficient
ρ = number density, N/V
ζ^* = reducing friction parameter
ρ^* = reduced density $N\sigma^3/V$

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