THE JOURNAL OF
PHYSICAL
CHEMISTRY A

© Copyright 2006 by the American Chemical Society VOLUME 110, NUMBER 3, JANUARY 26, 2006

FEATURE ARTICLE

Relations between Transport Coefficients and Their Density and Temperature Dependence

Byung Chan Eu

Department of Chemistry, McGill University, 801 Sherbrooke Street West,
Montreal, Quebec H3A 2K6, Canada

Received: August 29, 2005; In Final Form: November 1, 2005

Nonequilibrium statistical mechanics via density fluctuation theory predicts relations between the bulk and shear viscosity, thermal conductivity, and self-diffusion coefficient of a fluid. In this Feature Article, we discuss such relations holding for fluids over wide ranges of density and temperature experimentally studied in the laboratory. It is discussed how such relations can be used to successfully compute the density and temperature dependence on the basis of intermolecular interaction potential models with the help of the modified free volume theory and the generic van der Waals equation of state once the parameters in them are determined at a low density or at a subcritical temperature. Although some approximations have been made to derive them, they represent a reliable molecular theory of transport coefficients over the entire density and temperature ranges of fluids—namely, gases and liquids—a theory hitherto unavailable in the kinetic theory of liquids and dense gases.

1. Introduction

Linear transport coefficients, such as shear viscosity, bulk viscosity, thermal conductivity, and diffusion coefficients, are an important class of thermophysical properties of matter, which are indispensable for understanding the structure of matter and its thermophysical behavior, both near and far removed from equilibrium, and in engineering design of materials processing. A number of formal theories[1−7] have been developed for that purpose in nonequilibrium statistical mechanics and kinetic theory of gases and liquids in the past. However, in the dense gas and liquid density regimes these theories have not yielded the density and temperature dependence of the transport coefficients as was initially expected. The primary reason is that the desired results require accurate solutions of many-particle dynamics, but such solutions are not possible to obtain in closed form. For this reason, only the linear response theory, which is in a form more readily amenable to computer simulations, has been studied by applying molecular dynamics simulation (MDS) methods. Computer simulation methods, however, have their own limitations. In addition to the aforementioned problems, the plethora of thermophysical properties and, in particular, of transport coefficients tends to make their molecular understanding appear even more complex and daunting. Therefore the complex and difficult task would be made less daunting if there were some rigorous or sufficiently accurate relations between the various transport coefficients. One typical example for such relations is the Stokes−Einstein (SE) relation[8,9] that relates the (tracer) diffusion coefficient to the viscosity of the medium. However, the SE relation was derived by using methods of macroscopic physics and for particles of macroscopic size suspended in a continuous medium. If some relations akin to the SE relation can be derived for particles of molecular size by means of nonequilibrium statistical mechanics or the kinetic theory of dense gases and liquids, it will be extremely helpful for us to understand the thermophysical behavior of transport properties. In fact, such relations would even make it possible to examine the properties of transport coefficients semiempirically by using the information provided by one transport coefficient to study another with regard to the density and

10.1021/jp0548826 CCC: $33.50 © 2006 American Chemical Society
Published on Web 12/17/2005

Byung Chan Eu, a graduate of Seoul National University, received a Ph.D. degree in Chemical Physics from Brown University in 1965. From 1967 to 2001 he was on the faculty of McGill University, where he has been a professor emeritus of chemistry since September 2001. His recent research interests include kinetic theory of liquids and gases, nonequilibrium statistical mechanics and irreversible thermodynamics of systems far removed from equilibrium, generalized hydrodynamics, gas dynamics, and rheology of fluids.

temperature dependence. For transport processes in gases the Eucken relation[10] provides a typical example of such a relation.

In a recent series[11−22] of articles on transport coefficients of liquids, simple and complex, a nonequilibrium statistical mechanical theory, termed the density fluctuation theory, has been developed by the present author and his collaborator. The density fluctuation theory gives rise to relations between the potential energy part of transport coefficients and the self-diffusion coefficient of the fluid of interest that are reminiscent of the SE relation but with the coefficient factor quite different from that of the SE relation. Such relations have been used to successfully analyze[23−27] experimental data on the transport coefficients of simple as well as complex liquids, such as nitrogen and carbon dioxide, on the basis of an intermolecular potential model. In this Feature Article we would like to discuss such relations between transport coefficients of dense gases and liquids, which have been derived by means of nonequilibrium statistical mechanics and successfully validated through extensive comparison with experimental data with regard to their density and temperature dependence. Such relations provide us with a much sought molecular (statistical mechanical) theory of transport coefficients and their thermophysical behavior.

2. Eucken Relation and Ratio for Gases

2.1. Eucken Relation. The earliest example for the relation between transport coefficients, other than the SE relation, appears to be that of Eucken, who suggested on empirical grounds that the ratio of the thermal conductivity to the viscosity of a noble gas is a constant.[10] It is known as the Eucken relation[10,28]

$$\lambda_0 = f_{\mathrm{E}} C_v \eta_0 \tag{1}$$

where λ_0 and η_0 are the thermal conductivity and the viscosity of the gas, respectively, and C_v is the specific heat at constant volume. The factor f_{E} is known as the Eucken factor and has the value $^5/_2$ for noble gases. This relation is well verified experimentally and the kinetic theory based on the Chapman−Enskog method[28] supports it in reasonable accuracy. For polyatomic gases Eucken[10] suggested a decomposition of the factor f_{E} into translational and internal contributions $f_{\mathrm{E}} = f_{\mathrm{E}}^{\mathrm{tr}}(C_v^{\mathrm{tr}}/C_v) + f_{\mathrm{E}}^{\mathrm{int}}(C_v^{\mathrm{int}}/C_v)$, where C_v^{tr} and C_v^{int} were the translational and internal specific heat, respectively, and $f_{\mathrm{E}}^{\mathrm{tr}}$ and $f_{\mathrm{E}}^{\mathrm{int}}$ were, respectively, suggested to be $^5/_2$ and 1. Such values turned out to have only a limited range of applicability, and later authors made a number of improvements on the Eucken factor for polyatomic gases. Ubbelohde,[29] Hirschfelder,[30] and Mason and Monchick[31,32] were all associated with the improvements. We will find that this relation can be incorporated into a generalized relation that also holds in the liquid density regime.

Closely related to the Eucken relation is the relation between the thermal conductivity and the self-diffusion coefficient $D_0 \equiv D_{11}^0$, which may be written, in the Chapman−Enskog first approximation,[28] as

$$\lambda_0 = \frac{25}{6\sqrt{2}} \frac{W_1^{(2)}(1)}{W_1^{(2)}(2)} C_v \rho D_0 \tag{2}$$

and similarly for the shear viscosity

$$\eta_0 = \frac{5}{3\sqrt{2}} \frac{W_1^{(1)}(1)}{W_1^{(2)}(2)} \rho D_0 \equiv c\rho D_0 \tag{3}$$

In this expression, $\rho = mn$ with n denoting the number density and $W_1^{(l)}(r)$ given by[28]

$$W_1^{(l)}(r) = \int_0^\infty \mathrm{e}^{-\mathrm{g}^2} g^{2\mathrm{r}+2} \int_0^\infty (1 - \cos^l \chi) \frac{b}{\sigma}\, \mathrm{d}\left(\frac{b}{\sigma}\right) \mathrm{d}g^2 \tag{4}$$

where χ represents the classical scattering angle expressed by[33]

$$\chi = \pi - 2b \int_{r_0}^\infty \mathrm{d}R\, R^{-2} \left(1 - \frac{b^2}{R^2} - \frac{4v(R)}{mg^2}\right)^{-1/2} \tag{5}$$

In this expression for classical scattering angle, $v(R)$ is the intermolecular potential, which may be the Lennard-Jones potential

$$v(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$$

with the classical turning point r_0 defined by

$$1 - \frac{b^2}{{r_0}^2} - \frac{4v(r_0)}{mg^2} = 0$$

and b is the impact parameter. The integral $W_1^{(l)}(r)$ is computable once the scattering angle is known as a function of the impact parameter b and the relative speed g for the given intermolecular potential model. For hard spheres

$$W_1^{(l)}(r) = \frac{1}{4}(r + 1)!\left[2 - \frac{1 + (-1)^l}{l + 1}\right]$$

whereas for an inverse power law potential $v(R) = \kappa_{12}/R^\nu$ it follows from eqs 4 and 5 that $W_1^{(l)}(r) = A_l(\nu)\Gamma(r + 2 - 2/(\nu - 1))$ with $A_l(\nu) = \int_0^\infty (1 - \cos^l \chi) v\, \mathrm{d}v$.

The existence of relations 2 and 3 suggests that the time and spatial scales of thermal conduction and momentum transfer accompanying viscous flow in gases are set by diffusion of molecules, and that their scales are directly proportional to those of self-diffusion. For monatomic gases the Eucken relation may be regarded as a direct consequence of relations 2 and 3. It should be noted that, because ρD_0 is independent of density, the gas phase thermal conductivity and shear viscosity, λ_0 and η_0, are also independent of density, as is well-known experimentally in the normal density regime of gases.

For polyatomic molecules the kinetic theory results for the translational motion part of the transport coefficients may be written as[31]

$$\eta_0 = \frac{5}{16}\left(\frac{mk_BT}{\pi}\right)^{1/2}\frac{f_\eta}{\sigma^2\langle\Omega^{(2,2)*}\rangle} \tag{6}$$

$$\lambda_0 = \frac{75k_B}{64}\left(\frac{k_BT}{\pi m}\right)^{1/2}\frac{f_\lambda}{\sigma^2\langle\Omega^{(2,2)*}\rangle} = \frac{15k_B}{4m}\left(\frac{f_\lambda}{f_\eta}\right)\eta_0 \tag{7}$$

where f_η and f_λ are correction factors resulting from higher-order kinetic theory approximations, which differ from unity by at most a few percent. It should be noted that the thermal conductivity λ_0 in eq 7 is for the translational part only. Similarly, the self-diffusion coefficient D_{11} is given by the formula

$$D_{11} = \frac{3}{8n}\left(\frac{k_BT}{\pi m}\right)^{1/2}\frac{f_D}{\sigma^2\langle\Omega^{(1,1)*}\rangle} \equiv D_0 \tag{8}$$

where f_D has a meaning similar to f_η and f_λ and is close to unity. The symbols $\langle W^{(2,2)*}\rangle$ etc. denote the collision bracket integrals averaged over rotational angles of a polar molecule:

$$\langle\Omega^{(l,s)}*\rangle = \frac{1}{8\pi}\int_{-1}^{1}\int_{-1}^{1}\int_0^{2\pi} d\phi\ d(\cos\theta_1)\ d(\cos\theta_2)\ \Omega^{(l,s)}* \tag{9}$$

$$\Omega^{(l,s)}* = [(s+1)!]^{-1}\int_0^\infty d\gamma^2\ e^{-\gamma^2}\gamma^{2(s+1)}Q^{(l)}* \tag{10}$$

$$Q^{(l)}* = \frac{4(1+l)}{\sigma^2[2l-1-(-1)^l]}\int_0^\infty db\ b(1-\cos^l\chi) \tag{11}$$

According to Kihara's second approximation[31,34]

$$f_\eta = 1 + \frac{3}{196}[8\langle E^*\rangle - 7]^2 \qquad f_\lambda = \frac{14}{9}f_\eta - \frac{5}{9} \tag{12}$$

$$f_D = 1 + \frac{1}{8}[6\langle C^*\rangle - 5]^2[2\langle A^*\rangle + 5]^{-1} \tag{13}$$

with the definitions $\langle A^*\rangle = \langle\Omega^{(2,2)*}\rangle/\langle\Omega^{(1,1)*}\rangle$, $\langle C^*\rangle = \langle\Omega^{(1,2)*}\rangle/\langle\Omega^{(1,1)*}\rangle$, and $\langle E^*\rangle = \langle\Omega^{(2,3)*}\rangle/\langle\Omega^{(2,2)*}\rangle$. The Kihara approximation formulas are known to be fairly accurate. The relations involving the averaged collision bracket integrals are applicable to gases of polar molecules although they appear to be formulas for simple gases.

The relation between η_0 and $D_0 \equiv D_{11}$ for polar gases is therefore given by

$$\eta_0 = \frac{5}{6}\left(\frac{f_\eta}{f_D}\right)\frac{\langle\Omega^{(1,1)*}\rangle}{\langle\Omega^{(2,2)*}\rangle}\rho D_0 \equiv C\rho D_0 \tag{14}$$

where the constant C differs from the constant c in relation 3 for monatomic gases. Apart from the coefficient factors, relations 3 and 14 are the same with regard to the proportionality of η_0 to D_0, indicating that the momentum transfer associated with viscous phenomena is directly proportional to the mass transfer accompanying diffusion, and hence the time and spatial scales of the two transfer processes are directly related. This direct proportionality relation no longer holds in the liquid density regime and beyond, as will be seen.

2.2. Eucken Ratio. For want of appropriate terminology the ratio of bulk viscosity to shear viscosity will be referred to as the Eucken ratio. Because it was Eucken who considered the relation of shear viscosity and thermal conductivity for gases, the terminology seems appropriate. The first-order Chapman−Enskog theory predicts that monatomic gases have a vanishing bulk viscosity, but that is not the case for polyatomic gases[35] because of the presence of internal degrees of freedom into which the translational energy can be transferred, and vice versa. The bulk viscosity of a polyatomic gas is related to the shear viscosity, and the ratio of the bulk viscosity η_b^0 to the shear viscosity η_0,

$$f_r = \frac{\eta_b^0}{\eta_0} \tag{15}$$

may be a constant but is generally dependent on temperature. Such a relation can be practically rather useful because bulk viscosities are difficult to measure precisely, the only practical method being the method[36−38] of ultrasonic absorption and dispersion by the gas, but this method involves measuring a rather minor contribution attributable to the bulk viscosity of the entire ultrasonic absorption and dispersion spectra.[39] It is worth noting that Assael et al.[40] suggested a temperature independent form for f_r depending on molecular parameters only:

$$f_r \approx \frac{60\tau}{13\tau + 6} \tag{16}$$

where $\tau = 4I_R/m\sigma_R$ with σ_R denoting the diameter of the rough sphere and I_R its moment of inertia resulting from the internal distribution of mass within the sphere. For carbon dioxide the value of τ is estimated to be 0.048.

3. Relations for Transport Processes in Liquids

The relations of transport coefficients presented for processes in gases do not apply to those in liquids because momentum and energy transfers in liquids are accomplished in a fundamentally different manner than in gases. Because of its attractiveness the applicability[41,42] of the SE relation to particles of a molecular size has been tested by using experimental data on the viscosity and diffusion coefficient. However, such scrutinies have been inconclusive because in some cases the SE relation gives qualitatively reasonable correlations with experimental observations, whereas for some others it fails noticeably. A number of authors[43] have made statistical mechanical derivations of the SE relation, but after rather involved calculations, which tend to obscure the underlying physical process. Such relations in the liquid density regime therefore need appropriate fresh derivations by an entirely different route in the kinetic theory or nonequilibrium statistical mechanics of transport processes in liquids. We have been able to achieve the desired aim more definitively and quantitatively by means of the density fluctuation theory[11−14,16,22] and successfully validate[23−25,27] the relations with the help of experimental and MDS data.

3.1. Stokes−Einstein Relation. Despite its limitations the SE relation not only is frequently used but also contains valuable insights. Therefore it is worthwhile to examine how it is derived.

According to Stokes,[8] the kinetic (drag) force F_k acting on a sphere by the medium in which the sphere is immersed and moving at velocity v_s makes it possible to calculate the force if the appropriate hydrodynamic equations are solved.[44] It is found that the force F_k is given by $F_k = -a\eta\sigma v_s$, where σ is the radius of the sphere, $a = 6\pi$ for the stick boundary condition[44] (the medium sticks at the surface of the sphere in this boundary condition) and $a = 4\pi$ for the slip boundary condition[44] (the medium slips at the surface in this boundary condition), and η is the viscosity of the medium. Therefore the force exerted by the sphere on the medium F_s is given by $F_s = - F_k = a\eta\sigma v_s$.

In his theory of Brownian motion Einstein[9] considers a dilute suspension of ν macroscopic (colloidal) particles, which has an osmotic pressure $p = \nu k_B T$. Einstein regards the dynamic equilibrium as being brought about by two processes: (1) a movement of the suspended particle under the influence of the force F_s. (2) A process of diffusion arising from the irregular Brownian motion of the particles produced by the thermal agitation of molecules of the medium. By invoking the thermodynamic equilibrium condition, he obtains the dynamic (i.e., thermodynamic) equilibrium condition $\nu F_s = \partial p/\partial x = k_B T \partial\nu/\partial x$, if the particles are assumed to move in the direction of the x coordinate in the appropriately chosen coordinate system. The forces acting on ν particles generate a flux $\nu v_s = -\nu F_s/a\eta\sigma$, whereas the diffusion of the suspended particles produces the mass flux $\nu v_s = -D\partial\nu/\partial x$ in accordance with Fick's law.[45,46] Balancing the opposing forces and making use of the dynamic equilibrium condition he finds the SE relation

$$\eta = \frac{k_B T}{a\sigma D} \tag{17}$$

The salient feature of the derivation of the SE relation is the use of (1) the Navier−Stokes equations[44] to calculate the force on particles suspended in the medium and (2) Fick's law[45,46] of diffusion for the suspended particles, both of which are macroscopic equations. The transport coefficients are, of course, assumed to be known. Therefore there is no molecular theory provision for them in the SE relation. Nevertheless, Einstein additionally develops a stochastic theory of diffusion, which yields his well-known mean square displacement formula. Another important point to note is that D is evidently the tracer diffusion coefficient according to Einstein's derivation made by using the osmotic pressure of the suspension of Brownian particles. We will see that relations akin to the SE relation can be obtained for the potential energy part of transport coefficients in the liquid density regime by means of statistical mechanics, but they are not exactly the SE relation.

3.2. Density Fluctuation Theory and Relations between Transport Coefficients. The SE-like relations mentioned can be derived by means of nonequilibrium statistical mechanics, but by an approach radically different from the traditional route. The approach taken is the density fluctuation theory, and it is based on the following observation. As the density increases to the liquid density, voids created in the liquid play an increasingly important role, giving rise to strong density fluctuations over intermolecular distances. The momentum and energy transfer accompanying transport processes in liquids therefore become strongly dependent on density fluctuations, which are also modulated by diffusion of molecules over intermolecular distances. Consequently, the time and spatial scales of momentum and energy transfer attendant on the transport processes in liquids are set by the density fluctuations and diffusion of particles. The density fluctuation theory explicitly takes into account diffusion of particles over the range of intermolecular distance for the derivation of relations of transport coefficients mentioned. In the following, we describe how this aim can be achieved, but because of the space limitation, only the most salient examples for validation of the results will be given. It is the principal aim of this Feature Article.

3.2.1. Relation of Shear Viscosity to Self-Diffusion Coefficient: Simple Fluids Shear Viscosity. To obtain the statistical mechanical formula for shear viscosity, it is necessary to derive the constitutive relation for the shear stress in the fluid subjected to shearing externally applied. In principle, such a relation should be derived either from an appropriate kinetic equation,[6,7] as has been for relation 3 or 14, or by means of nonequilibrium statistical mechanics. In the liquid density regime the desired constitutive relation is obtained more readily in a more useful form if the shear stress tensor is calculated by using its statistical mechanical expression and taking density fluctuations and the structure of the liquid into account. The density fluctuation theory[11−14,16,22] of transport processes developed recently enables us to achieve the desired aim. Unlike the Chapman−Enskog method applied to the dense fluid kinetic equation (e.g., a generalized Boltzmann equation[6,7]) the density fluctuation theory takes into account the structure of liquids through density fluctuations, which give rise to density variation over intermolecular distances in the liquid. The density distribution function therefore may be expanded as a series in the density gradient. Eliminating the density gradient with the help of hydrodynamic equations and the constitutive equation[47] for the fluid velocity, it is possible to derive the Newtonian law of viscosity for the shear stress tensor, from which the statistical mechanical formula for the shear viscosity of the liquid can be derived. The formula so derived consists of a kinetic energy (dilute gas) part made up of relation 3 and a potential energy part similar to the SE relation. It has the form[11,13,47]

$$\eta = c\rho D_0 + \frac{\rho^2}{6D}\omega(n,T) \tag{18}$$

where $\omega(n,T)$, defined by

$$\omega(n, T) = \frac{2\pi}{15}\int_0^{r_{\max}} \mathrm{d}r\, r^5 v'(r)\, g(r,n,T)\, \theta(\xi - r) \tag{19}$$

contains the information on intermolecular interactions and the structure of the fluid. In this expression $v'(r) = \mathrm{d}v(r)/\mathrm{d}r$; $g(r,n,T)$ is the equilibrium pair correlation function; $\theta(x)$ is the Heaviside step function $\theta(x) = 1$ for $x > 0$ and 0 for $x < 0$; $r_{\max}$ is the range of the intermolecular force; ξ is the range of density fluctuations in the liquid; c is the constant factor appearing in eq 3; D_0 is the self-diffusion coefficient of the gas; and D is the self-diffusion coefficient of the pure liquid. The value of c, which is defined by eq 3, is approximately equal to unity. The density fluctuation range ξ, which, mathematically from the viewpoint of eq 19, may be regarded as the cutoff distance of the correlation range of $g(r)$, is not well defined but has a distribution $P(\xi)$. This distribution is believed to be a measure of random distribution of voids around radial position r from the point of attention in the liquid. It is assumed to be, as is usual for random distributions, a stretched exponential[48]

$$P(\xi) = \frac{\gamma\hat{\zeta}\xi^{\gamma-1}}{r^{\gamma}} \exp\left[-\hat{\zeta}(\rho,T)\left(\frac{\xi}{r}\right)^{\gamma}\right] \tag{20}$$

$$\int_0^{\infty} \mathrm{d}\xi \, P(\xi) = 1 \tag{21}$$

where $\hat{\zeta}(\rho,T)$ and γ are parameters to be chosen appropriately—it turns out γ does not explicitly appear in the formulas for the transport coefficients. Averaging formula 18 over the distribution $P(\xi)$ yields the formula for the observed shear viscosity, which will also be denoted by the same symbol[23,24,47] η, namely,

$$\eta = c\rho D_0 + \frac{\rho^2}{6D}\varpi(n,T) \exp[-\hat{\zeta}(\rho,T)] \tag{22}$$

where

$$\varpi(n,T) = \frac{2\pi}{15}\int_0^{r_{\max}} \mathrm{d}r \, r^5 v'(r) \, g(r,n,T) \tag{23}$$

The density fluctuation range ξ should evidently depend on T. If $T \gtrsim T_c$ (T_c = critical temperature), the density fluctuation range ξ should be roughly of the same order of magnitude as the range of the intermolecular force or larger, that is, $\xi \geq r_{\max}$. In that case, because $\theta(\xi - r) = 1$ in eq 19, it follows that

$$\hat{\zeta}(\rho,T) = 0 \qquad \text{for} \qquad T \gtrsim T_c \tag{24}$$

in eq 22. On the other hand, because the particles are more closely packed if $T < T_c$ than if $T > T_c$ and hence the density fluctuation range should be less than $r_{\max}$, the function $\hat{\zeta}(\rho,T)$ is not equal to zero but should depend on ρ. It therefore may be expanded in a series of ρ:

$$\hat{\zeta}(\rho,T) = \zeta_0 + \zeta_1\rho + \zeta_2\rho^2 + \cdots \tag{25}$$

where the coefficients ζ_0, ζ_1, ζ_2, etc. are parameters independent of T.

Whereas the first term on the right of eq 22 represents the dilute gas behavior of η, the second term represents the potential energy part of η and is reminiscent of the SE relation 17. The coefficients of the potential energy part of η, however, are quite different from those in the SE relation. Numerical comparisons show that these two relations have only a limited range of coincidence.[11,13,47] In any case, eq 22 is a generalization of eq 3 to the liquid density regime, which is a statistical mechanics-based relation between the shear viscosity and self-diffusion coefficient.

In the low-density regime the kinetic energy part of η is dominant whereas in the high (liquid) density regime the potential energy part becomes dominant. Thus the self-diffusion coefficient dependence and thus the density dependence smoothly cross over from one form to another as the density varies. Therefore eq 22 may be regarded as an interpolation formula with respect to the dependence on the self-diffusion coefficient of the fluid. It is a robust relation that accurately relates the two transport coefficients over wide ranges of temperature and density for simple (monatomic) fluids, as has been shown in the literature.[11,23,47] If the gas-phase self-diffusion coefficient D_0 is computed by means of the Chapman−Enskog theory,[28] if the self-diffusion coefficient D is computed by using the modified free volume (MFV) theory formula[16,18−21] 26 for diffusion given below, and if $g(r,n,T)$ is computed by a Monte Carlo (MC) method, then the shear viscosity can yield temperature and density dependence in excellent agreement with experiment over the entire ranges of temperature and density experimentally examined. For this purpose, the exponent $\hat{\zeta}(\rho)$, of course, must be empirically determined at an isotherm in the subcritical regime. In the supercritical regime of temperature such a procedure is unnecessary, and the formula becomes free from $\hat{\zeta}$ because $\hat{\zeta}(\rho) = 0$ in the supercritical regime of temperature.

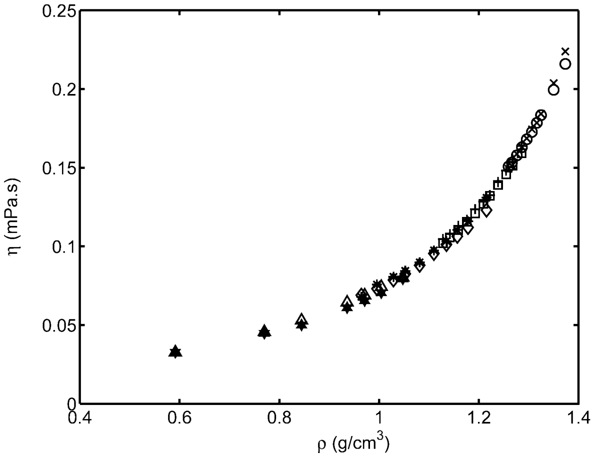

Figure 1. η vs ρ. The symbols are × (theory), ○ (exp) at T = 107 K; + (theory), □ (exp) at T = 125 K; * (theory), ◊ (exp) at T = 139 K; and ★ (theory), △ (exp) at T = 143 K. Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, B. C. Eu (*J. Phys. Chem. B* **2005**, *109*, 5873). Copyright 2005 American Chemical Society.

In connection with this manner of taking $\zeta(\rho,T)$, it should be remarked that the two different forms for $\hat{\zeta}(\rho,T)$ taken in the supercritical and subcritical regimes of temperature do not have such a sharp demarcation point at $T = T_c$, and it may be more useful in practice to continue to use the expansion in eq 25, especially in the supercritical regime near the critical point. This would be tantamount to making the coefficients ζ_i temperature-dependent. The present mode of expressing $\zeta(\rho,T)$ has been taken to make the theory free from the parameter ζ in the supercritical regime.

The relation for the shear viscosity, eq 22, has been extensively tested semiempirically[11,47] and also with the help[23,26,47] of the MFV theory and the GvdW equation of state—both of which make the theory molecular. For lack of space we can only present a couple of typical examples for argon and methane, which is usually treated[49] as a simple (spherical) liquid. In Figure 1, the shear viscosity of argon at temperatures T^* = 125 and 139 K is plotted against mass density ρ and compared with experimental data. For the comparison $\hat{\zeta} = 0.3890 + 0.5180\rho + 0.2578\rho^2$ was taken in the subcritical regime of temperature. For most thermophysical properties, methane has been successfully treated as a spherical molecule in the literature.[49] Therefore, by following tradition the shear viscosity of liquid methane has been examined by treating liquid methane as a simple liquid. Figure 2 is an example in which theoretical values of η are compared with experimental values for methane at various temperatures with $\hat{\zeta}$ represented by $\hat{\zeta} = 0.4992 + 2.655\rho + 0.33278\rho^2$ in the subcritical temperature regime. We emphasize that $\hat{\zeta} = 0$ in the supercritical regime. Figures 1 and 2 indicate the reliability and utility of relation 22.

Another type of relation between transport coefficients is that[6,26,47] between the non-Newtonian and Newtonian viscosities, which holds far removed from equilibrium in the high shear regime. This relation enables computation of the non-Newtonian

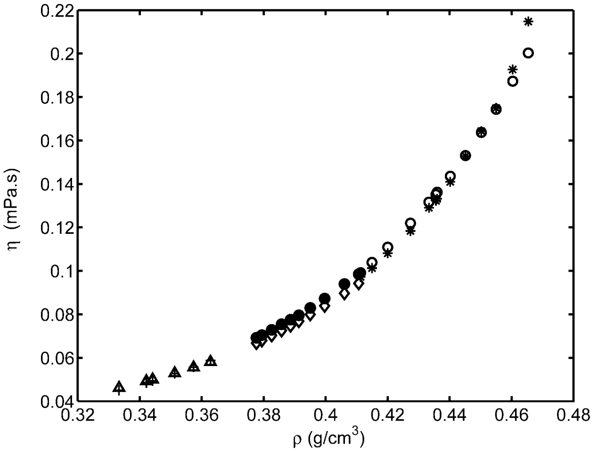

Figure 2. η vs ρ for liquid methane. The symbols are * (theory), ○ (experiment) at $T = 120$ K; ● (theory), ◇ (experiment) at $T = 140$K; + (theory), △ (experiment) at $T = 180$ K. Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, B. C. Eu (*J. Phys. Chem. B* **2005**, *109*, 5873). Copyright 2005 American Chemical Society.

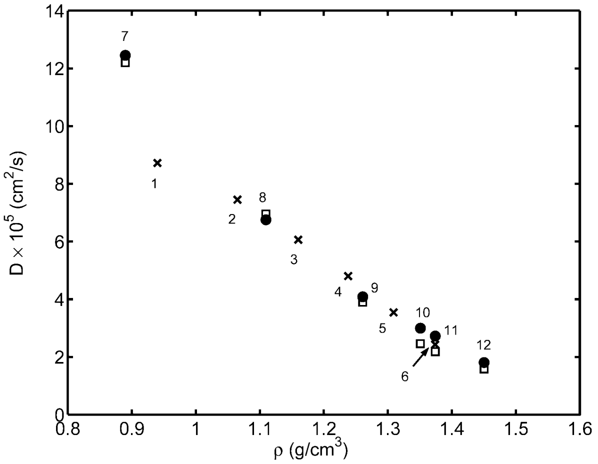

Figure 3. D vs ρ at various temperatures. ●, theory; □, MDS data; ×, experiment of Naghizadeh and Rice.[57] Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, B. C. Eu (*J. Phys. Chem. B* **2005**, *109*, 5873). Copyright 2005 American Chemical Society.

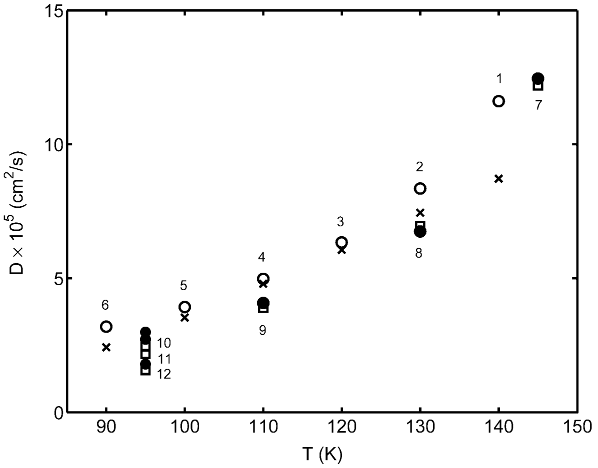

Figure 4. D vs T for argon at various isochores. ●, ○, MFV theory: □, MDS data: ×, experimental data. Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, B. C. Eu (*J. Phys. Chem. B* **2005**, *109*, 5873). Copyright 2005 American Chemical Society.

viscosity, given the Newtonian viscosity of a fluid. Although quite relevant and useful in the study of rheology,[6,50] discussion of such a relation will be deferred to ref 26.

The self-diffusion coefficient D in eq 22 can be determined by performing computer simulations for the mean square displacement of the particles. It can be also computed if the MFV theory for diffusion is utilized, together with the generic van der Waals (GvdW) equation of state,[47,51,52] which can be computed with $g(r,n,T)$. According to the MFV theory,[16,18−21] D is given by

$$D = 1.019\frac{3}{8\rho\sigma^2}\sqrt{\frac{k_BT}{\pi m}}\exp\left(-\frac{\vartheta v^*}{v_f}\right) \qquad (26)$$

where the preexponential factor is the self-diffusion coefficient of hard spheres,[28] ϑ is the free volume overlap parameter, v_f is the mean free volume, and v^* is the minimum free volume activating diffusion. The product $v_0 \equiv \vartheta v^*$ defines the critical free volume facilitating diffusion of particles. It may be calculated by a suitable model for the minimum size of voids, activating diffusion in the liquid.

In most free volume theories in the literature[53−56] v_f is treated as an empirical parameter, but in the MFV theory it can be given a precise statistical mechanical representation. According to the GvdW equation of state[47,51,52] the statistical mechanical expression for v_f is given by

$$v_f = v\left[1 - \frac{2\pi n}{3k_BT}\int_0^\sigma dr\, r^3 v'(r)\, g(r,n,T)\right]^{-1} \qquad (27)$$

in terms of the pair correlation function, which contains the information on the structure of the liquid and the intermolecular force. Here σ (e.g., the diameter of the hard sphere) is the point at which $v(r) = 0$ and $g(r,n,T)$ can be calculated by an MC simulation method. The self-diffusion coefficient of the MFV theory presented earlier has been rather thoroughly examined in comparison[16,18−21,23−25] with experimental and MDS data. The numerals in Figures 3 and 4 denote different isotherms: 1 = 140; 2 = 130; 3 = 120; 4 = 110; 5 = 100; 6 = 90; 7 = 145; 8 = 130; 9 = 110; 10 = 95; 11 = 95; 12 = 95 K. In Figure 3, the MFV theory results of the density dependence of D at various temperatures are compared in excellent agreement with experimental[57] and MDS[58] data. In Figure 4, the MFV theory results of the temperature dependence of D at various densities are compared with both experimental[57] and MDS data.[58] Because the values of D obtained from the MFV theory are reliable, we may also expect that the shear viscosity values will be equally reliable: as a matter of fact, this expectation has already been fulfilled, as has been shown in Figures 1 and 2. Figure 4 shows that the theory and the MDS data agree well throughout the density range considered. The experimental point (×) significantly deviates from both the theory and the MDS data at the high-temperature regime. It might be possible that the experiment was not as accurate in the high-temperature regime as at intermediate temperatures.

Therefore with the help of the MFV theory and the GvdW equation of state the Newtonian shear viscosity of monatomic liquids can be calculated in terms of D_0 and $g(r,n,T)$ as a function of n and T once the intermolecular interaction potential is specified. Relation 22, eq 26, and eq 27 constitute a robust molecular theory of shear viscosity.

3.2.2. Relation of Bulk Viscosity to Self-Diffusion Coefficient: Simple Fluids. The bulk viscosity is related to the excess normal stress, which, if the fluid is compressed in the direction of the z axis, may be written as $\Delta = {}^2/_3(P_{xx} - P_{zz})$, where P_{xx} and P_{zz} are respectively the tangential and longitudinal components of the pressure (stress) tensor **P** in the fluid. In contrast to the bulk viscosity, the shear viscosity is related to the offdiagonal element P_{xy} of the pressure tensor. Therefore, being related to the same **P**, both bulk and shear viscosities share the same physical mechanism for momentum transfer, which is responsible for viscous transport phenomena. This means that the basic ideas of the density fluctuation theory for the shear viscosity can be applied to the bulk viscosity[12,14] of simple fluids. However, because the bulk viscosity η_b of dilute monatomic gases is equal to zero at the first-order Chapman–Enskog theory level, it consists entirely of the potential energy contribution[47]

$$\eta_b = \frac{\rho^2}{9D}\varpi(n,T)\exp[-\hat{\xi}(\rho,T)] \tag{28}$$

Therefore, by making use of the shear viscosity formula 22, the bulk viscosity η_b can be related to shear viscosity η by

$$\eta_b = \frac{2}{3}\left(1 - c\frac{\rho D_0}{\eta}\right)\eta \tag{29}$$

This relation is a generalization of eq 15 to simple liquids. The bulk viscosity is generally deduced by measuring ultrasonic absorption and dispersion[36−38] by the fluid, but because the contribution of the bulk viscosity to the absorption and dispersion spectra is relatively small compared to the shear viscosity contribution, the measurement of bulk viscosity entails a sizable uncertainty. Relation 29 therefore can be useful for avoiding the experimental uncertainty in measuring η_b because shear viscosity can be experimentally determined in high precision.

Experiment[59−62] shows that the ratio η_b/η is in the range 0.85−0.56. If the second term on the right of eq 29 is ignored, the ratio is approximately 0.67. Therefore relation 29 can be used to estimate the bulk viscosity with reasonable accuracy from information on the shear viscosity and the Chapman–Enskog prediction for the gas self-diffusion coefficient D_0.

Formula 28 has been shown to give good values,[12,47] qualitatively and quantitatively, for the bulk viscosity of simple fluids, such as argon, krypton, and xenon. Because the coefficient of the Eucken ratio 29 was also found to be reasonable and the behavior of the shear viscosity is in good agreement with experiment, as noted earlier, relation 29 is expected to, and does, yield a correct bulk viscosity; the space limitation compels us to omit graphical presentation for η_b. Validation of relation 29 is available for monatomic fluids in ref 12.

3.2.3. Relation of Thermal Conductivity to Self-Diffusion Coefficient: Simple Fluids. Energy transfer in space is the dynamical cause for the thermal conduction in the fluid. As it is for momentum transfer accompanying viscous phenomena, energy transfer in liquids is strongly influenced by density fluctuations arising from the creation of voids and the variation of voids in space, as the fluid becomes dense. It has been shown that density fluctuation theory is also applicable to thermal conduction, and the thermal conductivity λ of a simple fluid is given by the formula[27,47]

$$\lambda = f_E C_v \eta_0 + \frac{\rho^2}{6D}\langle\chi\rangle\exp[-\hat{\xi}(\rho,T)] \tag{30}$$

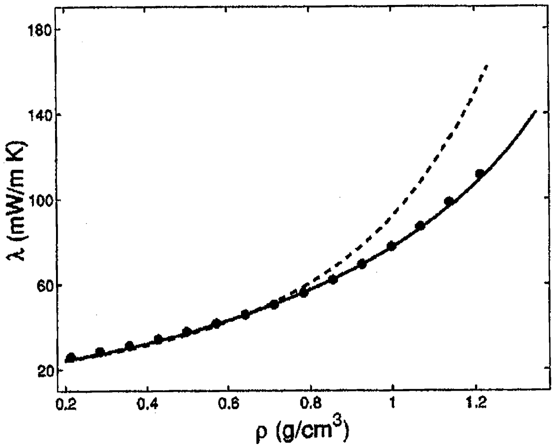

Figure 5. λ vs ρ for argon at $T = 348.15$ K. The solid curve is the theory with κ^* given by eq 34 and the broken curve is the theory with $\kappa^* = 0.4$. The symbols represent the experimental data. Reproduced with permission from K. Rah and B. C. Eu (*J. Chem. Phys.* **2001**, *115*, 9370). Copyright 2001 American Institute of Physics.

where $\hat{\xi}(\rho,T)$ has the same meaning as for the bulk and shear viscosities, η_0 is the gas shear viscosity appearing in eq 3, and

$$\langle\chi\rangle = \chi_v + \chi_\omega \tag{31}$$

$$\chi_v = -\frac{4\pi k_B\kappa^*}{m}\int_0^{r_{\max}} \mathrm{d}r\, r^4 v(r)\, g(r,n,T) \tag{32}$$

$$\chi_\omega = \frac{4\pi k_B\kappa^*}{5m}\int_0^{r_{\max}} \mathrm{d}r\, r^5 v'(r)\, g(r,n,T) \tag{33}$$

$$\kappa^* = a_0\frac{\alpha T}{1 + 2\alpha T} \tag{34}$$

with α denoting the isobaric expansion coefficient of the fluid and a_0 an adjustable parameter that is approximately equal to 1.2. The first term on the right of eq 25 represents the kinetic energy part λ_0 of λ describing the low-density behavior of the thermal conductivity—Eucken relation for gas—whereas the second term is the potential energy part, which also looks similar to the SE relation. The dynamical reason for this similarity lies in the fact that the time and spatial scales of energy transfer accompanying thermal conduction in the liquid are set by density fluctuations and diffusion of particles over intermolecular distances. By making use of the shear viscosity formula 22, the formula for the thermal conductivity can be also written as

$$\lambda = f_E C_v\left(1 + \frac{\langle\chi\rangle}{f_E C_v \varpi}\right)\eta_0 + \frac{\langle\chi\rangle}{\varpi}\eta \tag{35}$$

This relation is obviously a generalization to the liquid density regime of the Eucken relation 1 for gas-phase transport processes discussed earlier.

Apart from the theoretical implication of the existence of a common dynamical mechanism for the potential energy parts of the thermal conduction and viscous phenomena in the liquid density regime, the relation by itself can be quite useful at the practical level because it makes it possible to compute the thermal conductivity from the information on the shear viscosity in the gas and liquid density regimes of the fluid, which is easier to measure with good accuracy than is the self-diffusion coefficient. Relation 30 or 35 has been applied to calculate the thermal conductivity of monatomic fluids such as argon, xenon, and krypton in excellent agreement with experiment.

Figure 5 shows the density dependence of the thermal conductivity of argon: $T = 348.15$ K is well above the critical

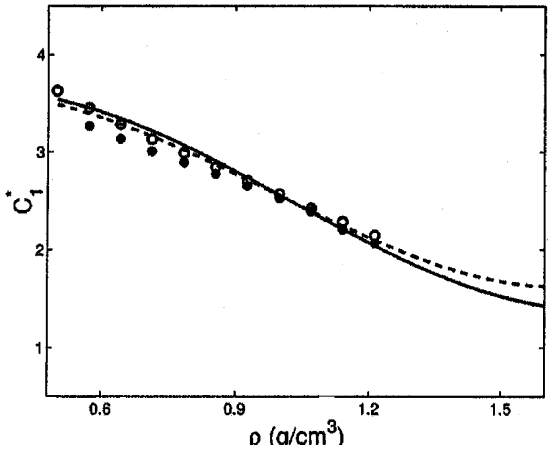

Figure 6. $C_1^* = \chi/\omega$ at two isotherms. The curves are theoretical: —, at $T = 298$ K; - - -, at $T = 348$ K. The symbols are for the experimental data by Michels et al.[63] Reproduced with permission from K. Rah and B. C. Eu (*J. Chem. Phys.* **2001**, *115*, 9370). Copyright 2001 American Institute of Physics.

temperature $T_c = 150.86$ K for argon, so that $\hat{\zeta} = 0$ for this case. It should be noted that $\kappa^* = 0.4$ is the low-density limiting value of κ^*, which was taken for the broken curve in Figure 5. Therefore the density dependence of the isobaric expansion coefficient α in κ^* becomes important as the density increases. The generalized Eucken relation for simple fluids is tested in Figure 6 by using $C_1^* = \chi/\omega$, because this quantity is identical with the ratio $\langle\chi\rangle/\varpi$ and made parameter-free because $T = 348.15$ K is well above T_c and thus $\hat{\zeta} = 0$. Comparison with experimental data[63] indicates that the generalized Eucken relation is well obeyed by liquid argon. Together with relation 22 and formulas 26 and 27, relation 20 or 30 forms a reliable molecular theory of thermal conductivity of simple liquids.

3.2.4. Relation of Tracer Diffusion Coefficient to Self-Diffusion Coefficient. The density fluctuation theory employed to obtain the relations between the viscosities, or thermal conductivity, and the self-diffusion coefficient presented earlier does not yield a relation between the diffusion coefficients of a mixture and the self-diffusion coefficient. The desired relation, however, can be obtained by means of the MFV theory[16,18−21] of diffusion in a mixture. For this purpose it is first necessary to apply the ideas underlying the MFV theory of a pure substance to a fluid mixture. For a binary mixture the MFV theory yields the diffusion coefficient D_{12} in the form[17]

$$D_{12} = D_{12}^0 \exp\left(-\frac{\vartheta v_{12}^*}{v_f}\right) \tag{36}$$

where v_{12}^* is the minimum free volume facilitating diffusion, ϑ is a parameter characterizing the free volume overlap, and

$$D_{12}^0 = \frac{3}{8\rho{\sigma_{12}}^2}\sqrt{\frac{k_BT(m_1+m_2)}{2m_1m_2}} \tag{37}$$

with $\rho = \rho_1 + \rho_2$. The product of factors $v_{12}^c \equiv \vartheta v_{12}^*$ may be regarded as the critical free volume activating diffusion in the mixture. The mean free volume may be calculated with the help of the GvdW equation of state for the mixture[18,19,47]

$$[p + A(n, T)n^2][1 - B(n, T)n] = nk_BT \tag{38}$$

where A and B are defined by the formulas

$$A = \sum_{i,j=1}^{2} A_{ij}X_iX_j \tag{39}$$

$$B = \frac{\sum_{i,j=1}^{2} B_{ij}X_iX_j}{1 + n\sum_{i,j=1}^{2} B_{ij}X_iX_j} \tag{40}$$

$$A_{ij}(n,T) = \frac{2\pi}{3}\int_{\sigma_{ij}}^{\infty}\mathrm{d}r\, r^3 v'_{ij}(r)\, g_{ij}(r,n,T) \tag{41}$$

$$B_{ij}(n,T) = -\frac{2\pi}{3k_BT}\int_0^{\sigma_{ij}}\mathrm{d}r\, r^3 v'_{ij}(r)\, g_{ij}(r,n,T) \tag{42}$$

with X_i denoting the mole fraction of species i and σ_{ij} the point at which $v_{ij}(r) = 0$, where $v_{ij}(r)$ is the potential energy of pair ij. By using the GvdW equation of state 38, we obtain the statistical mechanical representation of mean free volume per molecule[47]

$$\begin{aligned} v_f &= v[1 - B(n,T)n] \\ &= v\left[1 - \frac{2\pi n}{3k_BT}\sum_{i,j=1}^{2} X_iX_j\int_0^{\sigma_{ij}}\mathrm{d}r\, r^3 v'_{ij}(r)\, g_{ij}(r)\right]^{-1} \end{aligned} \tag{43}$$

This statistical mechanical formula makes it possible to compute the mean free volume from a knowledge of pair correlation functions $g_{ij}(r,n,T)$. An MC simulation method[64] provides $g_{ij}(r,n,T)$, given the intermolecular forces. The critical free volume for a binary mixture may be expressed in the form

$$v_{12}^c \equiv \vartheta v_{12}^* = \vartheta_1 v_1^* X_1 + \vartheta_2 v_2^* X_2 \tag{44}$$

where $\vartheta_i v_i^*$ ($i = 1, 2$) is the critical free volume for species i. The tracer diffusion coefficient $D_t(2)$ for species 2 is then obtained from eq 36 by taking the limit $X_2 \rightarrow 0$:

$$D_t(2) = D_{12}^0 \exp\left(-\frac{\vartheta_1 v_1^*}{v_f}\right) \tag{45}$$

From eq 36 the self-diffusion coefficient $D_1 \equiv D_{11}$ of the solvent species 1 can also be obtained in the form

$$D_1 = \frac{3}{8\rho{\sigma_1}^2}\sqrt{\frac{k_BT}{m_1}}\exp\left(-\frac{\vartheta_1 v_1^*}{v_f}\right) \tag{46}$$

Taking the ratio of $D_t(2)$ to D_1 the relation of $D_t(2)$ and D_1 is obtained:

$$D_t(2) = \sqrt{\frac{1 + m_1/m_2}{2}}\left(\frac{2}{1 + \sigma_2/\sigma_1}\right)^2 D_1 \equiv R_s D_1 \tag{47}$$

This formula enables us to compute the diffusion coefficient of the tracer solute from the knowledge of the self-diffusion coefficient of the solvent. The validity of this relation has been extensively and successfully tested[20] for mixtures of organic compounds on application of the Bondi−Edward rule[65,66] for estimating the van der Waals radii of complex organic molecules. Relation 47, however, is not expected to be applicable to large tracer particles such as colloids suspended in a medium

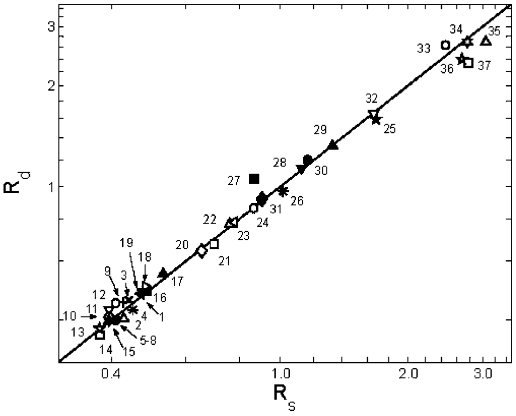

Figure 7. $R_d = D_t/D_1$ vs R_s when solvent effects are assumed negligible. Reproduced with permission from K. Rah, S. Kwak, B. C. Eu, and M. Lafleur (*J. Phys. Chem. A* **2002**, *106*, 11841). Copyright 2002 American Chemical Society.

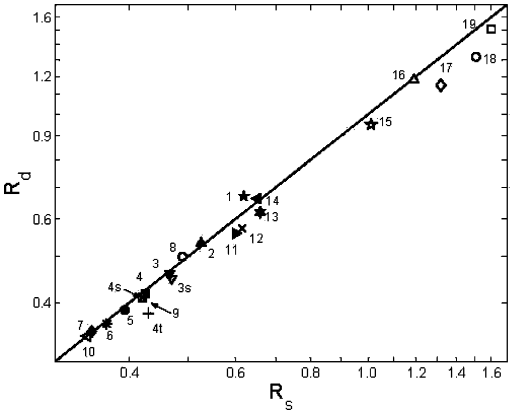

Figure 8. $R_d = D_t/D_1$ vs R_s when solvent effects are present. Reproduced with permission from K. Rah, S. Kwak, B. C. Eu, and M. Lafleur (*J. Phys. Chem. A* **2002**, *106*, 11841). Copyright 2002 American Chemical Society.

of much smaller particles. For such systems free volume theory would require significant modifications.

In Figures 7 and 8, the ratio $R_d = D_t/D_1$ is plotted against R_s computed with the Bondi−Edward rule for estimating the van der Waals radii of various organic solutes examined. The arabic numerals stand for various organic compounds examined, which are common laboratory chemicals. The names of the compounds are too numerous to list here: interested readers are referred to the original paper[20] and to ref 47 for a listing of them. The important point is that relation 47 allows computation of the tracer diffusion coefficient from a knowledge of the self-diffusion coefficient of the solvent, and vice versa, according to the MFV theory employed to derive relation 47. In view of the biological and biochemical relevance of the chemical compounds examined, it is expected that relation 47 may have considerable practical utility.

4. Generalization of the Relations to Complex Fluids

The relations presented for simple liquids in the previous section can be generalized to complex liquids. The problem is tantamount to generalizing the density fluctuation theory of transport processes in simple liquids, the MFV theory of diffusion, and the GvdW equation of state to complex liquids. It was found that this aim could be adequately achieved if the site−site interaction model was employed for the interaction potentials of the complex liquids. In this model the nonbonded atoms or groups in complex molecules interact with each other through spherically symmetric pairwise-additive potentials, e.g., Lennard-Jones potentials, whereas the bonded atoms or groups are either bonded at a fixed distance or interact through a Morse or harmonic potential. Particularly for hydrocarbons or polymers we may assume a freely jointed chain of beads interacting through pairwise-additive Lennard-Jones potentials. Generalization[13,14,47,52] of density fluctuation theory has been made for rigid homonuclear diatomic or linear molecules of two identical interaction sites. In such a model the potential energy contributions to the transport coefficients, shear and bulk viscosity and thermal conductivity, remain remarkably the same in form as those for monatomic (i.e., simple) liquids, except that the site−site pair correlation functions should be calculated appropriately for the site−site pairs of interest by means of either an integral equation theory[67] or an MC simulation method.[64] The MVF theory of diffusion and the GvdW equation of state should be also modified appropriately. With the aforementioned allowance in the difference of the meaning of the pair correlation function appearing in the formula for the mean free volume v_f and in the expression for ϖ for the viscosities or $\langle\chi\rangle$ for the thermal conductivity the relations of transport coefficients for rigid molecules of homonuclear interaction sites are formally the same as those already presented for monatomic liquids, eqs 22, 28, and 30. Of course, the kinetic energy parts of the formulas mentioned should be appropriately calculated with the diatomic molecular versions,[35] which have been already discussed in section 2, or with polyatomic versions.[35,68] Diatomic and polyatomic transport cross sections of dilute gases are rather time-consuming and difficult to calculate precisely. However, in the high-density regime the kinetic energy contributions to the transport coefficients, such as η_0 and λ_0, are small compared to the potential energy contributions, so that for all practical purposes one may simply use the transport cross sections averaged over rotational angles of molecules. If this approximation is used, then it is possible to use the transport coefficients for dilute spherical molecules with the diameters of the molecules appropriately adjusted.

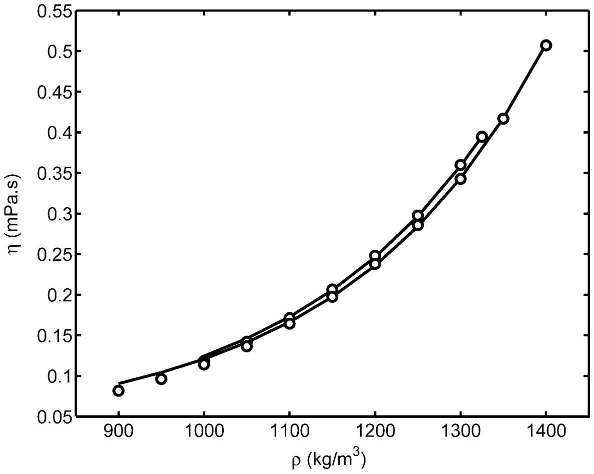

Figure 9. η vs ρ for carbon dioxide at $T = 260$ K (upper curve) and 290 K (lower curve). The solid curves are the experimental results of ref 69, whereas the open circles are theoretical results of ref 24. Reproduced with permission from A. Eskandari Nasrabad, R. Laghaei, B. C. Eu (*J. Phys. Chem. B* **2005**, *109*, 8171). Copyright 2005 American Chemical Society.

The density dependence of the shear viscosity of carbon dioxide at $T = 260$ K and $T = 290$ K is shown in Figure 9. The solid curves are experimental data represented by a fitting formula of Fenghour et al.,[69] whereas the symbols are theoretical values computed from relation 22 appropriately generalized to a rigid two-interaction-site molecular fluid modeling carbon

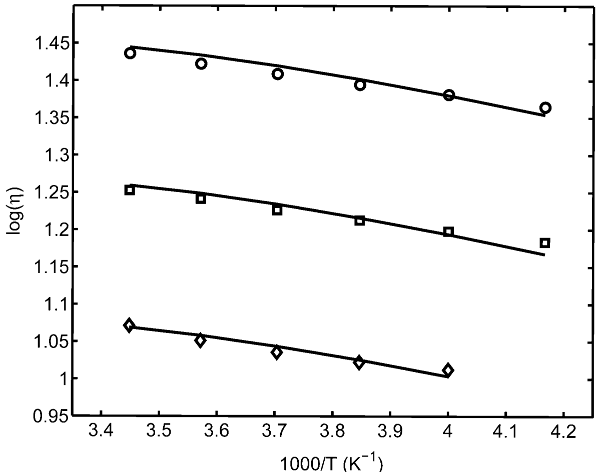

Figure 10. η vs T for carbon dioxide at $\rho = 1.20$ g cm^{-3} (upper curve), $\rho = 1.25$ g cm^{-3} (middle curve), and $\rho = 1.30$ g cm^{-3} (lower curve). The curves represent the experimental results from ref 69, whereas the symbols represent the theoretical results of ref 24. Reproduced with permission from A. Eskandari Nasrabad, R. Laghaei, and B. C. Eu (*J. Phys. Chem. B* **2005**, *109,* 8171). Copyright 2005 American Chemical Society.

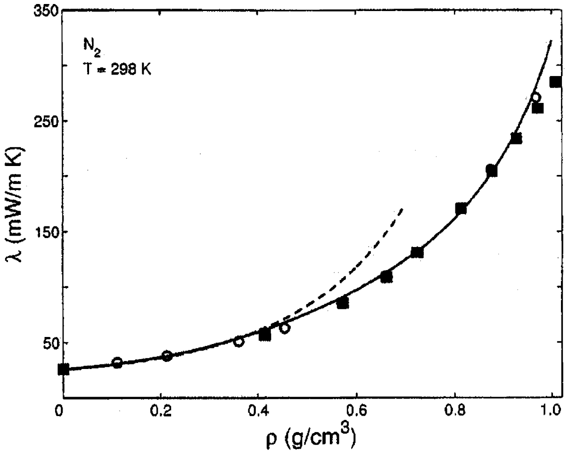

Figure 11. λ vs ρ for nitrogen at $T = 298$ K.The symbols represent the experimental data: ○, Younglove;[70] □, Le Neindre et al.[71] The solid curve is the theoretical result with κ^* given by eq 34 and the broken curve is the theoretical result with $\kappa^* = 0.56$. Reproduced with permission from K. Rah and B. C. Eu, (*J. Chem. Phys.* **2002**, *117,* 4386). Copyright 2002 American Institute of Physics.

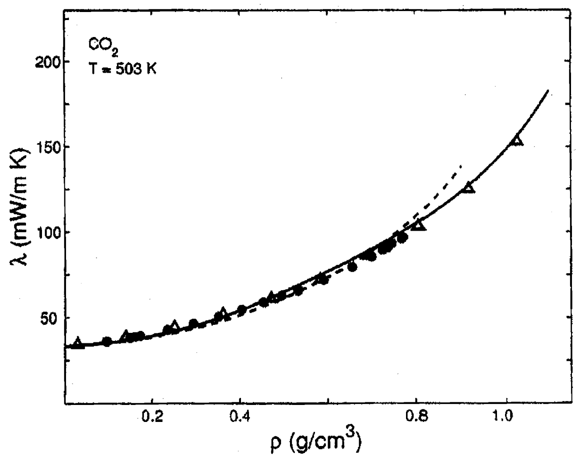

Figure 12. λ vs ρ for carbon dioxide at $T = 470$ K.The symbols represent the experimental data: ○, Younglove[70]; ●, Le Neindre et al.;[71] △, by Vesovic et al.[72] The meanings of the curves are the same as for Figure 11. Reproduced with permission from K. Rah and B. C. Eu (*J. Chem. Phys.* **2002**, *117,* 4386). Copyright 2002 American Institute of Physics.

dioxide. The value of $\hat{\zeta}$ is equal to zero in the supercritical region and is obtained from the formula $\hat{\zeta} = 4.70 - 8.51\rho + 3.86\rho^2$ in the subcritical region. The temperature dependence of η predicted by the theory is examined for three isochores in Figure 10. The curves represent experimental data obtained from the fitting formula of Fenghour et al.,[69] and the symbols are the theoretical predictions of the theory.[24] The theory presented for rigid two-interaction-site molecular fluids was also tested for liquid nitrogen and found to yield excellent results for the density and temperature dependence in comparison with experiment. For the thermal conductivity of rigid two-interaction-site molecular fluids, we have available only thermal conductivities computed with the generalized Eucken relation. In Figure 11, the thermal conductivity of nitrogen at $T = 298$ K ($> T_c = 126.2$ K) is shown as a function of density. The solid curve is the theory with κ^* given by eq 34 and the broken curve is the theoretical prediction with $\kappa^* = 0.56$. The symbols represent experimental data.[70,71] In Figure 12, the thermal conductivity of carbon dioxide at $T = 470$ K ($> T_c = 304.1$ K) is plotted against density. The meanings of the curves are the same as for Figure 11, and the symbols represent experimental data.[71,72] For these two figures experimental values were used for λ_0 because of the difficulty of calculating precise values of λ_0 for diatomic gases. Because good values for D are not available in the literature and the MFV theory for D was not previously available, the diatomic fluid version of the generalized Eucken relation, eq 35, was utilized to calculate the thermal conductivity of diatomic fluids. These comparisons clearly validate not only the generalized Eucken relation used but also the underlying relation between λ and the self-diffusion coefficients D_0 and D—that is, the density fluctuation theory. Application of the MFV theory of diffusion and GvdW equation of state for diatomic fluids to calculate the thermal conductivity of carbon dioxide from the generalized density fluctuation formula is recently made[73] successfully. The results of the study will be reported soon.

If the two interaction sites in the rigid molecules are not identical, that is, the rigid molecules are not homonuclear, then ϖ and $\langle\chi\rangle$ must be replaced by

$$\varpi \Rightarrow \sum_{i,j=1}^{2} \varpi_{i,j} \qquad \langle\chi\rangle \Rightarrow \sum_{i,j=1}^{2} \langle\chi\rangle_{ij} \tag{48}$$

where

$$\varpi_{ij}(\rho,T) = \frac{2\pi}{15}\int_0^{r_{\max ij}} \mathrm{d}r\, r^5 v'_{ij}(r)\, g_{ij}(r,n,T) \tag{49}$$

$$\langle\chi\rangle_{ij} = \chi_{vij} + \chi_{\omega ij} \tag{50}$$

$$\chi_{vij} = -\frac{4\pi k_B \kappa^*}{m}\int_0^{r_{\max ij}} \mathrm{d}r\, r^4 v_{ij}(r)\, g_{ij}(r,n,T) \tag{51}$$

$$\chi_{\omega ij} = \frac{4\pi k_B \kappa^*}{m}\int_0^{r_{\max ij}} \mathrm{d}r\, r^5 v'_{ij}(r)\, g_{ij}(r,n,T) \tag{52}$$

with m denoting the molecular mass. Generalization of these relations to more complicated polyatomic liquids, such as polymeric liquids, is not available at present. They are obviously a subject that should be studied in the future.

5. Concluding Remarks

The problem of correctly calculating the density and temperature dependence of transport coefficients of dense gases and liquids from a molecular interaction model has been a long standing challenge in statistical mechanics. In recent years, the challenge has been increasingly met with MDS methods, but MDS methods also have their own limitations. It is not an exaggeration that the aforementioned problem has been one of the principal motivations for developing the kinetic theory of dense gases and liquids, and there have been numerous investigations in various directions made in the past to calculate transport properties[74] and relations[43,75] between macroscopic properties by using kinetic theory methods.[1−7] Because these investigations follow the traditional route in kinetic theory by which macroscopic quantities are expressed in many-particle collision operators of one kind or another, they all require a systematic solution of many particle dynamics for the collision operators involved. For example, Mehaffey and Cukier[43b] employ a dense fluid kinetic theory, in which collisions are treated with repeated ring diagrams for many-particle collisions, and deduce an SE-like relation. Owing to the difficulty in obtaining a practical and correctly behaved solution of many-particle dynamics, such kinetic theory approaches have not yielded density and temperature dependence of transport coefficients of liquids that can be compared with experiment.

In the density fluctuation theory, many-particle dynamics does not appear in the form of a many-particle collision operator but is implicit in the self-diffusion coefficient and the equilibrium pair correlation function. And the self-diffusion coefficient can be deferred to a separate treatment by another theory, for example, the MFV theory of diffusion. Interestingly, the MFV theory enables us to avoid directly solving many-particle collision dynamics unlike the aforementioned kinetic theory approaches. A combination of the density fluctuation theory, the MVF theory of diffusion, and the GvdW equation of state has thus provided us with a practical and accurate molecular theory of transport coefficients, which yields reliable values for them once the equilibrium pair correlation functions have been suitably calculated by either an integral equation theory or an MC simulation method. Because the latter yields rather accurate results efficiently, it is preferable. In this connection, it should be remarked that MC simulation methods cannot be applied to calculate dynamical quantities such as autocorrelation functions appearing in the linear response theory or transport coefficients appearing in the traditional kinetic theory. The present theory therefore is different from the aforementioned kinetic theories and MDS or nonequilibrium MDS methods in that with only an MC simulation method the transport coefficients can be calculated in good accuracy over wide ranges of density and temperature. It is a tremendous advantage that solution of many-particle collision dynamics can be effectively replaced by an MC simulation method, which involves no subtleties encountered in nonequilibrium MDS methods or is not as time-consuming as MDS methods.

The set of four transport coefficients D, η, η_b, and λ, however, contains three parameters α, a_0, and ζ—although less than one for each transport coefficient—which, once determined either at the low density limit or with a subcritical isotherm, remain applicable to all densities and temperatures. Although derived in approximations, the relations of transport coefficients enable us to compute in good accuracy the density and temperature dependence of transport coefficients over the entire density and temperature regimes experimentally studied with the so determined parameters and with an MC simulation method for $g(r)$ alone.

The aforementioned relations have been successfully validated by comparisons with experimental data available in the literature, as has been shown in this article by using salient examples. We are now thus in possession of an approximate, but practical, molecular theory of transport coefficients of dense gases and liquids, which enables us to compute and comprehend the properties of transport coefficients both for simple fluids and for complex fluids such as diatomic fluids. The theory points the way to treat the relations in better approximations and also for more complex fluids, but this task is left for future work.

Acknowledgment. This work was supported in part by the grants from the Natural Sciences and Engineering Research Council of Canada. I would like to thank Drs. K. Rah, R. Laghaei, and A. Eskandari Nasrabad for the collaborations on the works featured in this article and Mazen Al-Ghoul for useful comments.

References and Notes

(1) Enskog, D. *Kungl. Svenska Vetenskaps Akad. Handl.* **1921**, *63*, 4.
(2) Rice, S. A.; Boon, J. P.; Davis, H. T. In *Simple Dense Fluids*; Frisch, H. L., Salsburg Z. W., Eds.; Academic: New York, 1968; pp 251−404.
(3) Green, M. S. *J. Chem. Phys.* **1952**, *20*, 1281; **1954**, *22*, 398.
(4) Kubo, R. *J. Phys. Soc. Jpn.* **1957**, *12*, 570.
(5) Eu, B. C. *Ann. Phys.* **1979**, *118*, 187, 230; **1979**, *120*, 423.
(6) Eu, B. C. *Kinetic Theory and Irreversible Thermodynamics*; Wiley: New York, 1992.
(7) Eu, B. C. *Nonequilibrium Statistical Mechanics; Ensemble Method*; Kluwer: Dordrecht, The Netherlands, 1998.
(8) Stokes, G. G. *Mathematical and Physical Papers*; Cambridge U. P., London, 1880; Vol. 1, pp 38−43.
(9) Einstein, A. *Brownian Movement*; Dover: New York, 1956.
(10) Eucken, A. *Phys.. Z* **1913**, *14*, 324.
(11) Rah, K.; Eu, B. C. *Phys. Rev. E* **1999**, *60*, 4105.
(12) Rah, K.; Eu, B. C. *Phys. Rev. Lett.* **1999**, *83*, 4566.
(13) Rah, K.; Eu, B. C. *J. Chem. Phys.* **2000**, *112*, 7118.
(14) Rah, K.; Eu, B. C. *J. Chem. Phys.* **2001**, *114*, 10436.
(15) Rah, K.; Eu, B. C. *J. Chem. Phys.* **2001**, *115*, 2634.
(16) Rah, K.; Eu, B. C. *J. Chem. Phys.* **2001**, *115*, 9370.
(17) Rah, K.; Eu, B. C. *Phys. Rev. Lett.* **2002**, *88*, 065901.
(18) Rah, K.; Eu, B. C. *J. Chem. Phys.* **2002**, *116*, 7967.
(19) Rah, K.; Kwak, S.; Eu, B. C.; Lafleur, M. *J. Phys. Chem. A* **2002**, *106*, 11841.
(20) Rah, K.; Eu, B. C. *Mol. Phys.* **2002**, *100*, 3281.
(21) Rah, K.; Eu, B. C. *J. Chem. Phys.* **2002**, *117*, 4386.
(22) Rah, K.; Eu, B. C. *Phys. Rev. E* **2003**, *68*, 051204.
(23) Laghaei, R.; Eskandari Nasrabad, A.; Eu, B. C. *J. Phys. Chem. B* **2005**, *109*, 5873.
(24) Eskandari Nasrabad, A.; Laghaei, R.; Eu, B. C. *J. Phys. Chem. B* **2005**, *109*, 8171.
(25) Laghaei, R.; Eskandari Nasrabad, A.; Eu, B. C. *J. Phys. Chem. B* **2005**, *109*, 21375.
(26) Laghaei, R.; Eskandari Nasrabad, A.; Eu, B. C. *J. Chem. Phys.*, submitted for publication.
(27) Laghaei, R.; Eskandari Nasrabad, A.; Eu, B. C. *J. Chem. Phys.* **2005**, *123*, December 1 issue.
(28) Chapman, S.; Cowling, T. G. *The Mathematical Theory of Nonuniform Gases*, 3rd ed.; Cambridge University Press: London, 1970.
(29) Ubbelohde, A. R. *J. Chem. Phys.* **1935**, *3*, 219.
(30) Hirschfelder, J. O. *J. Chem. Phys.* **1957**, *26*, 274, 282.
(31) (a) Monchick, L.; Mason, E. A. *J. Chem. Phys.* **1961**, *35*, 1676. (b) Mason, E. A.; Rice, W. E. *J. Chem. Phys.* **1954**, *22*, 843.
(32) Mason, E. A.; Monchick, L. *J. Chem. Phys.* **1962**, *36*, 1622.
(33) Goldstein, H. *Classical Mechanics*; Addison-Wesely: Reading, MA, 1959.
(34) (a) Kihara, T. *Rev. Mod. Phys.* **1953**, *25*, 831. (b) Kihara, T. *J. Stat. Phys.* **1975**, *13*, 137.
(35) McCourt, F. R. W.; Beenakker, J. J. M.; Köhler, W. E.; Kuscer, I. *Nonequilibrium Phenomena in Polyatomic Gases*; Clarendon: Oxford, U.K., 1990; Vol. 1.
(36) Greenspan, M. *J. Acoust. Soc. Am.* **1959**, *31*, 155.
(37) Herzfeld, K. F.; Litovitz, T. A. *Absorption and Dispersion of Ultrasonic Waves*; Academic: New York, 1959.
(38) Sluijter, C. G.; Knaap, H. E. P.; Beenakker, J. J. M. *Physica* **1964**, *30*, 745. Prangsma, G.; Alberga, J. A. H.; Beenakker, J. J. M. *Physica* **1973**, *64*, 284. van Houten, H. L.; Hermans, J. F.; Beenakker, J. J. M. *Physica A* **1985**, *131*, 64.
(39) Eu, B. C.; Ohr, Y. G. *Phys. Fluids* **2001**, *13*, 744.
(40) Assael, M. J.; McCourt, F. R.; Maitland, G. C.; Mustafa, M.; Wakeham, W. *High Temperature-High Pressure* **1998**, *17*, 291.

(41) Parkhurst, H. J.; Jonas, J. *J. Chem. Phys*. **1975**, *63*, 2705. Fury, M.; Munie, G.; Jonas, J. *J. Chem. Phys.* **1979**, *70*, 1260.

(42) Pollack, G. *Phys. Rev. A* **1981**, *23*, 2660; Pollack, G. L.; Enyeart, J. *Phys. Rev. A* **1985**, *31*, 980.

(43) (a) Keyes, T.; Oppenheim, I. *Phys. Rev. A* **1973**, *8*, 937. (b) Mehaffey, J. R.; Cukier, R. I. *Phys. Rev. A* **1978**, *17*, 1181. (c) Zwanzig, R. *J. Chem. Phys.* **1983**, *79*, 4507.

(44) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; Wiley: New York, 1960; pp 513−515. Lamb, H. *Hydrodynamics*, 6th ed.; Cambridge University Press: London, 1975; Chapter XI.

(45) de Groot, S. R.; Mazur, P. *Nonequilibrium Thermodynamics*; North-Holland, Amsterdam, 1962.

(46) Eu, B. C. *Generalized Thermodynamics: Thermodynamics of Irreversible Processes and Generalized Hydrodynamics*; Kluwer: Dordrecht, 2002.

(47) Eu, B. C. *Transport Coefficients of Fluids*; Springer, Heidelberg, 2006.

(48) Shlesinger, M. F.; Montroll, E. W. *Proc. Nat. Acad. Sci. U.S.A.* **1984**, *81*, 1280.

(49) Setzmann, U.; Wagner, W. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1061.

(50) Barnes, H. A.; Hutton, J. F.; Walters, K. *An Introduction to Rheology*; Elsevier: Amsterdam, 1989.

(51) Eu, B. C.; Rah, K. *Phys. Rev. E* **2001**, *63*, 031203.

(52) Rah, K.; Eu, B. C. *J. Phys. Chem. B* **2003**, *107*, 4382.

(53) Eyring, H. *J. Chem. Phys.* **1936**, *4*, 283. Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

(54) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.

(55) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471.

(56) Cohen, M. H.; Turnbull, D. *J. Chem. Phys*. **1959**, *31*, 1164.

(57) Naghizadeh, J.; Rice, S. A. *J. Chem. Phys.* **1961**, *36*, 2710.

(58) Ermakova, E.; Solca, J.; Huber, H.; Welker, M. *J. Chem. Phys.* **1995**, *102*, 4942.

(59) Naugle, D. G.; Lunsford, J. H.; Singer, J. R. *J. Chem. Phys.* **1966**, *45*, 4669.

(60) Naugle, D. G. *J. Chem. Phys.* **1966**, *44*, 741.

(61) Cowan, J. A.; Ball, R. N. *Can. J. Phys.* **1972**, *50*, 1881.

(62) Malbrunot, P.; Boyer, A.; Charles, E.; Abachi, H. *Phys. Rev. A* **1983**, *27*, 1523.

(63) Michels, A.; Sengers, J. V.; van de Lundert, L. J. M. *Physica* **1963**, *29*, 149.

(64) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon, Oxford, 1987.

(65) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(66) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261.

(67) Farhat, H.; Eu, B. C. *J. Chem. Phys.* **1996**, *104*, 300.

(68) Ferziger, J. H.; Kaper, H. G. *Mathematical Theory of Transport Processes in Gases*; North-Holland, Amsterdam, 1975.

(69) Fenghour, A.; Wakeham, W. A.; Vesovic, V. *J. Phys. Chem. Ref. Data* **1998**, *27*, 31.

(70) Younglove, B. A. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 1.

(71) Tufeur, R.; Le Neindre, B. *Int. J. Thermophys.* **1980**, *1*, 375.

(72) Vesovic, V.; Wakeham, W. A.; Olchowy, G. A.; Sengers, J. V.; Watson, J. T. R.; Millat, J. *J. Phys. Chem. Ref. Data* **1990**, *19*, 763.

(73) Laghaei, R.; Eskandari Nasrabad, A. Eu, B. C. Manuscript in preparation.

(74) van Beijeren, H.; Dorfman, J. R. *J. Stat. Phys.* **1980**, *23*, 335.

(75) Bocquet, L.; Piasecki, J.; Hansen, J.-P. *J. Stat. Phys.* **1994**, *76*, 505.