Modified Free Volume Theory of Self-Diffusion and Molecular Theory of Shear Viscosity of Liquid Carbon Dioxide

Afshin Eskandari Nasrabad, Rozita Laghaei, and Byung Chan Eu*

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

In previous work on the density fluctuation theory of transport coefficients of liquids, it was necessary to use empirical self-diffusion coefficients to calculate the transport coefficients (e.g., shear viscosity of carbon dioxide). In this work, the necessity of empirical input of the self-diffusion coefficients in the calculation of shear viscosity is removed, and the theory is thus made a self-contained molecular theory of transport coefficients of liquids, albeit it contains an empirical parameter in the subcritical regime. The required self-diffusion coefficients of liquid carbon dioxide are calculated by using the modified free volume theory for which the generic van der Waals equation of state and Monte Carlo simulations are combined to accurately compute the mean free volume by means of statistical mechanics. They have been computed as a function of density along four different isotherms and isobars. A Lennard-Jones site−site interaction potential was used to model the molecular carbon dioxide interaction. The density and temperature dependence of the theoretical self-diffusion coefficients are shown to be in excellent agreement with experimental data when the minimum critical free volume is identified with the molecular volume. The self-diffusion coefficients thus computed are then used to compute the density and temperature dependence of the shear viscosity of liquid carbon dioxide by employing the density fluctuation theory formula for shear viscosity as reported in an earlier paper (*J. Chem. Phys.* **2000,** *112,* 7118). The theoretical shear viscosity is shown to be robust and yields excellent density and temperature dependence for carbon dioxide. The pair correlation function appearing in the theory has been computed by Monte Carlo simulations.

1. Introduction

Carbon dioxide not only plays an important role in environmental phenomena but also is important as a solvent in a wide variety of industrial processes. One of its rapidly growing applications is supercritical fluid extraction in agricultural, pharmaceutical, and other fields, where separation and purification of products are very important. In such industrial applications, the knowledge of the transport properties of the solvent is vital for design and optimization of engineering processes. On the experimental side, much effort has been made in the literature to measure transport coefficients of carbon dioxide[1−11] by means of various methods. Moreover, some research workers have used molecular dynamics simulation methods to study its thermophysical properties on the basis of a model for the molecule.[12,13]

In a series of papers[14−18] on the transport coefficients of liquids, one of us (B.C.E.) and his collaborator developed a density fluctuation theory on the basis of nonequilibrium statistical mechanics. According to the theory, the viscosity and thermal conductivity of liquids can be shown to consist of kinetic and potential energy contributions. Moreover, the potential energy contribution, which is given in terms of the intermolecular forces between the particles, the equilibrium pair correlation function, and the self-diffusion coefficient of the liquid, is rather reminiscent of the well-known Stokes−Einstein (SE) relation.[19] The expressions obtained for the transport coefficients have forms that enable us to perform completely molecular theoretical calculations for the transport coefficients if the quantities involved, such as the self-diffusion coefficient and the equilibrium pair correlation function, are calculated by means of statistical mechanics on the basis of intermolecular forces.

However, since at the time when the theory was developed it was not possible to calculate the self-diffusion coefficient in the aforementioned formulas by means of a molecular theory other than molecular dynamics simulation methods, the experimental or molecular dynamics simulation data for self-diffusion coefficients available in the literature were employed to calculate the shear viscosity and thermal conductivity of liquids such as argon, neon, xenon, and rigid diatomic molecular liquids such as nitrogen and carbon dioxide. The comparison of the theoretical results thus obtained for the transport coefficients was found to be excellent in accuracy with regard to their density and temperature dependence over the entire experimentally studied range once the parameter appearing in the formula (i.e., the cutoff parameter for the interaction range) was adjusted suitably at a single subcritical temperature. However, since self-diffusion coefficients either experimentally measured or computed by molecular dynamics simulation methods were used for such calculations of the transport coefficients, the theory became semiempirical, but the removal of the semiempiricism of the theory arising from the necessity of using empirical self-diffusion coefficients was left for future work when a reliable theory of self-diffusion coefficients comes into being for the fluids of interest.

In the intervening time, we have discovered a canonical equation of state in the form of a generic van der Waals equation

* Author to whom correspondence should be addressed. Phone: (514) 398-6929. Fax: (514) 398-3797. E-mail: Byung.Eu@McGill.Ca.

of state,[20−22] into the form of which the virial equation of state can be transformed, and with the generic van der Waals (GvdW) equation of state it has been possible to obtain a rigorous statistical mechanical representation of the mean free volume, which has been defying a precise statistical mechanical definition. Such representation of the mean free volume turns out to be a crucial component of the theory for self-diffusion coefficients, which removes the necessity for the empirical input of self-diffusion coefficients in the density fluctuation theory as mentioned.

Cohen and Turnbull[23] in 1959 developed a free volume theory of diffusion for the purpose of studying glass forming substances. In this theory, the empirical Doolittle form[24] was derived for the self-diffusion coefficient. The derived formula was expressed in terms of the mean free volume in addition to a number of other incompletely determined parameters. Determination of the mean free volume was a major problem among other parameters in the theory. Since the aforementioned GvdW equation of state has made it possible to perform a well-defined statistical mechanical computation for the mean free volume, we have been able to modify the Cohen−Turnbull (CT) free volume theory into a reasonable molecular theory.[25−28] The CT theory of diffusion thus modified will be termed the modified free volume (MFV) theory of diffusion. It has been shown in comparison with experiment or computer simulation data on diffusion that the MFV theory of diffusion yields reliable density and temperature dependence for diffusion coefficients over wide density and temperature ranges. In a recent work,[29] we have shown how the parameter for the free volume overlap, which is inherent to the CT theory and the MFV theory, and the parameter that appears in the transport coefficients, such as viscosity and thermal conductivity, in connection with the density fluctuation range in the fluid, can be determined with the help of the experimental data of either viscosity or thermal conductivity at a single subcritical temperature. (It should be noted that the viscosity formula is free from the aforementioned parameter in the supercritical temperature range.) And once the parameters are suitably determined at a temperature, the combination of the density fluctuation theory of transport coefficients and the MFV theory of diffusion provides us with a molecular theory of transport coefficients of liquids, which is able to account rather accurately for the density and temperature dependence of the transport coefficients of the liquids experimentally studied. Apart from the parameters mentioned, the theory therefore is fully implementable on the basis of intermolecular forces and statistical mechanics only. In this paper, we show that the aforementioned theory can be also applied successfully to rigid molecular liquids such as carbon dioxide. In the present work, the equilibrium pair correlation functions necessary for calculating the mean free volume in the MFV theory of diffusion have been obtained by means of a Monte Carlo simulation method.

In section 2, with carbon dioxide as an example and modeled as a rigid rotor, the density fluctuation theory of shear viscosity is briefly described, and the formula for the shear viscosity is presented in terms of the self-diffusion coefficient and the equilibrium pair correlation functions of the liquids as well as the intermolecular forces between the interaction sites of molecules. In this section, we also briefly review the GvdW equation of state and the MFV theory of diffision. The Monte Carlo simulation method employed is also described in this section. In section 3, the theoretical self-diffusion coefficient and shear viscosity of carbon dioxide are compared with experimental data and also with computer simulation results,

whenever the latter are available in the literature. In section 4, concluding remarks are given.

2. Brief Description of the Density Fluctuation Theory of Shear Viscosity

We assume that for the purpose of calculating thermophysical properties, which are not related to spectroscopic properties, carbon dioxide may be regarded as a rigid molecule with two interaction sites. This model would considerably simplify the theory. In this model, the intramolecular forces responsible for bonding are absent, and the shear stress tensor consists of only the contributions arising from translational momentum transfers and the virial tensor arising from the intermolecular site−site interactions. Thus, the stress tensor $\mathbf{P}(\mathbf{r},t)$ at position $\mathbf{r}$ within the fluid at time t consists of the kinetic and potential energy parts

$$\mathbf{P}(\mathbf{r},t) = \mathbf{P}_k(\mathbf{r},t) + \mathbf{P}_v(\mathbf{r},t) \tag{1}$$

where the kinetic part $\mathbf{P}_k(\mathbf{r},t)$ and the potential energy part $\mathbf{P}_v(\mathbf{r},t)$ are, respectively, given by

$$\mathbf{P}_k(\mathbf{r},t) = \int d\mathbf{P}_c \int d\mathbf{p}_{12} \int d\mathbf{r}_{12} \, MCC f\,(\mathbf{P}_c,\mathbf{r},\mathbf{p}_{12},\mathbf{r}_{12};t) \tag{2}$$

$$\mathbf{P}_v(\mathbf{r},t) = -\frac{1}{2} \int_0^1 d\lambda \int d\mathbf{R} \, \frac{\mathbf{RR}}{R} V'(R) \times$$
$$\rho^{(2)}(\mathbf{r} - \lambda\mathbf{R},\mathbf{r} + (1-\lambda)\mathbf{R};t) \tag{3}$$

In these expressions, $\mathbf{P}_c$ and $\mathbf{p}_{12}$ are the center of mass momentum and the relative momentum of sites 1 and 2 of the molecule, respectively, and $\mathbf{r}_{12}$ is the relative distance conjugate to $\mathbf{p}_{12}$. M is the mass of the molecule, $\mathbf{C}$ denotes the peculiar velocity defined by $\mathbf{C} = \mathbf{P}_c/M - \mathbf{u}$ with $\mathbf{u}$ denoting the fluid velocity, and $f\,(\mathbf{P}_c,\mathbf{r},\mathbf{p}_{12},\mathbf{r}_{12};t)$ denotes the singlet distribution function of carbon dioxide at time t. The expression for the kinetic part $\mathbf{P}_k(\mathbf{r},t)$ of the stress tensor in eq 2 is the result of applying approximations related to the contributions from the intramolecular motion in carbon dioxide, which becomes legitimate if the molecule is assumed to be rigid and the coupling between the shearing motion and the molecular rotation is neglected since the latter contributes to a higher-order effect. In eq 3, $\mathbf{R}$ denotes the relative distance between interaction sites on two different molecules, $V(R)$ is the site−site interaction potential energy, which will be assumed to be a Lennard-Jones potential; λ is the Kirkwood charging parameter,[30,31] and $\rho^{(2)}(\mathbf{r},\mathbf{r}',t)$ denotes the dynamic pair distribution function at time t

$$\rho^{(2)}(\mathbf{r},\mathbf{r}',t) = M^{-2}\rho(\mathbf{r},t)\rho(\mathbf{r}',t)g(\mathbf{r},\mathbf{r}',t) \tag{4}$$

where $\rho(\mathbf{r},t)$ denotes the mass density at $\mathbf{r}$ and at t and $g(\mathbf{r},\mathbf{r}',t)$ is the dynamic radial distribution function. The shear stress tensor $\Pi(\mathbf{r},t)$ is the traceless symmetric parts of $\mathbf{P}_k(\mathbf{r},t)$ and $\mathbf{P}_v(\mathbf{r},t)$

$$\Pi(\mathbf{r},t) = \Pi_k(\mathbf{r},t) + \Pi_v(\mathbf{r},t)$$
$$\equiv [\mathbf{P}_k(\mathbf{r},t)]^{(2)} + [\mathbf{P}_v(\mathbf{r},t)]^{(2)} \tag{5}$$

where the symbol $[\mathbf{A}]^{(2)}$ denotes

$$[\mathbf{A}]^{(2)} = \frac{1}{2}(\mathbf{A} + \mathbf{A}^t) - \frac{1}{3}\delta \, \text{Tr} \, \mathbf{A}$$

with δ denoting the unit second rank tensor. The shear viscosity η of the fluid is then defined by the Newtonian law of viscosity

$$\Pi(\mathbf{r},t) = -2\eta[\nabla\mathbf{u}]^{(2)} \tag{6}$$

where $[\nabla\mathbf{u}]^{(2)}$ gives the shear rate. The stress tensor as split in eq 5 suggests that the shear viscosity may be also split into two parts, kinetic and potential

$$\eta = \eta_k + \eta_v \tag{7}$$

where η_k stands for the kinetic part arising from the kinetic part of the stress tensor $\Pi_k(\mathbf{r},t)$ whereas η_v denotes the potential energy part arising from the potential part of the stress tensor $\Pi_v(\mathbf{r},t)$. These two parts of the shear viscosity have diametrically opposite behaviors with respect to density and temperature, characteristic of gases and liquids, respectively. Thus, it may be said that the viscosity expressed as in eq 7 is an interpolation formula, which describes the crossover behavior of η from that of the gas to that of the liquid. We will see that this is indeed the case, since one overwhelms the other in magnitude as the density varies from the gas (low-density) regime to the liquid (high-density) regime, and vice versa. This crossover behavior is regulated by the self-diffusion coefficient, which sets time and spatial scales of transport processes and strongly depends on density and temperature.

According to the density fluctuation theory,[14-18] the kinetic part η_k is given by the Chapman–Enskog shear viscosity of the dilute gas made up of the molecules of interest. Since the kinetic part η_k is well known, it is not of primary interest to us here and will be discussed when the theory is compared with experiment. However, the potential energy part η_v is given by the statistical mechanical formula

$$\eta_v = \frac{\rho^2 \omega(\rho,T)}{6D} \tag{8}$$

where

$$\omega(\rho,T) = \frac{2\pi}{15} \int_0^\infty dr\ r^5 V'(r) g(r,\rho,T) \theta(\xi - r) \tag{9}$$

The parameter ξ gives the density fluctuation range in the nonequilibrium liquid subjected to shearing, and it is generally less than the range of intermolecular force r_{max}. It is not possible to fix this parameter within the framework of the density fluctuation theory. Therefore it remains an adjustable parameter, but it was empirically found[16] that it is directly related to the size of the molecule of interest. Since it is not well determined, it is appropriate to introduce a distribution function for ξ, which will be denoted by $P(\xi)$ defined in the range $0 \leq \xi < \infty$. Averaging eq 8 over this distribution of ξ, we obtain the viscosity formula

$$\eta_v = \frac{\rho^2 \langle\omega(\rho,T)\rangle}{6D} \tag{10}$$

where

$$\langle\omega(\rho,T)\rangle = \frac{2\pi}{15} \int_0^\infty d\xi \int_0^\infty dr\ r^5 V'(r) g(r,\rho,T) \theta(\xi - r) P(\xi) \tag{11}$$

with $P(\xi)$ denoting the distribution function for the range of density fluctuations around the position r in the liquid. (Note that this position r is the radial coordinate of the second particle of the pair of particles of interest here. The other is located at

the origin of the coordinate system.) The distribution function $P(\xi)$ is assumed to be in the stretched exponential form[32,33]

$$P(\xi,\rho,T) = \frac{\gamma\zeta(\rho,T)\xi^{\gamma-1}}{r^\gamma} \exp\left[-\zeta(\rho,T)\left(\frac{\xi}{r}\right)^\gamma\right] \tag{12}$$

where $\zeta(\rho,T)$ is a function of ρ and T that describes the width of the ξ distribution. This distribution function gives a measure of voids around position r in the liquid where density tends to fluctuate because of the voids. This distribution function probably can be estimated by means of computer simulations for the structure of the liquid, but in this work we will treat it as an empirical quantity, which may be deduced from the experimental data on transport properties, such as shear viscosity and thermal conductivity. We will find that the information on $\zeta(\rho,T)$ can be inferred from the experimental data on the shear viscosity.

On performing integration over ξ, we obtain η_v in the form

$$\eta_v = \frac{\rho^2}{6D} \hat{\omega}(\rho, T)\, e^{-\zeta(\rho,T)} \tag{13}$$

where

$$\hat{\omega}(\rho,T) = \frac{2\pi}{15} \int_0^\infty dr\ r^5 V'(r) g(r,\rho,T) \tag{14}$$

It should be remarked that this integral is practically limited to $r \leq r_{max}$, the range of intermolecular force, because the integral gets a rather small contribution for the range of $r > r_{max}$. Upon combining eq 13 with the kinetic part η_k, we obtain the shear viscosity formula

$$\eta = \eta_k + \frac{\rho^2}{6D} \hat{\omega}(\rho,T)\, e^{-\zeta(\rho,T)} \tag{15}$$

where η_k is given by the Chapman–Enskog shear viscosity formula[34,35] for the rigid two-interaction-site molecule (rotator) at normal density.

According to the Boltzmann kinetic theory,[34,35] η_k is proportional to the dilute gas self-diffusion coefficient and independent of density. Therefore, the dependences on the self-diffusion coefficient of η_k and η_v are inverse to each other.

Notice that the potential energy part of η is reminiscent of the SE relation between the viscosity of a continuous medium and the diffusion coefficient for a large particle diffusing through the medium. Despite the similarity, it is not the SE relation because of the difference in the coefficient factor; the present formula does not require the particle to be macroscopic as does the SE relation.[19] Apart from the factor $\zeta(\rho,T)$, the formula (eq 15) does not contain parameters other than the potential parameters if the self-diffusion coefficient D can be calculated by means of statistical mechanics on the basis of intermolecular forces. In the previous works[14-18] on the density fluctuation theory of transport coefficients, we have employed experimental or molecular dynamics simulation data on D to compute the density and temperature dependence of the shear viscosity. In this work, we propose to calculate D by applying the MFV theory of diffusion.[25-28] In this way, the density fluctuation theory is made fully molecular except for the parameter $\zeta(\rho,T)$ or ξ. In the previous works [14-18,29] mentioned earlier, it was empirically found that although the value of ξ becomes less than the range of the interaction potential energy r_{max} if the temperature is well below the critical temperature, it becomes equal to or larger than r_{max} if the temperature is near or above

the critical temperature of the fluid. Therefore, in the super-critical temperature regime, we may set $\zeta(\rho,T) = 0$. Consequently, in the supercritical temperature regime, the theory becomes free from the parameter ζ and thereby is rendered implementable on the basis of intermolecular forces only. It was also found[16] that the parameter ξ is directly related to the bond length of the molecule, suggesting that it has a close relation to the structure of the liquid. Therefore, it is expected that the parameter ζ in the subcritical regime should be dependent on density; we believe that it is a measure of the variation of voids with respect to density in the subcritical regime. Unfortunately, since it is not possible to calculate the density dependence of ζ by means of statistical mechanics at present, it must be treated as an empirical parameter. Nevertheless, this parameter seems to provide information on the void distribution around a particle in the liquid. Fortunately, once this parameter is fixed at a subcritical temperature, the shear viscosity formula with the same form for ζ is applicable to all other temperatures. In this sense, for the given liquid the theory becomes predictive on the basis of intermolecular forces only.

2.1. Generic van der Waals Equation of State. The van der Waals equation of state[36] was historically a breakthrough in the thermodynamics of liquid and gas phases. Despite less than perfect quantitative results and some glaring defects, it offers a powerful tool to study the phase transition phenomena and the thermodynamics of fluids. In the van der Waals theory, the thermophysical properties of the fluid are expressible in terms of two mean quantities, one related to the volume excluded by the molecules and the other related to the mean attraction between molecules. With the two aforementioned parameters, the van der Waals equation of state has the simple mathematical representation

$$(p + a'\rho^2)(1 - b'\rho) = \rho\beta^{-1} \qquad (16)$$

where p is the pressure, ρ is the density, $\beta = 1/k_B T$ with k_B denoting the Boltzmann constant and T the temperature, and a' and b' are the van der Waals constants. Much effort has been made in the literature to improve this form of the equation of state so as to acquire better qualitative and quantitative results for the thermodynamic description of fluids (for a complete discussion see ref 37).

In a recent paper by Eu and Rah,[20] it has been shown that the van der Waals equation of state (eq 16) is a limiting case of the canonical form of the equation of state since the former is recovered from the latter as $\rho \rightarrow 0$ and $T \rightarrow \infty$. The canonical form was called the generic van der Waals equation of state because it has exactly the same form as the original van der Waals equation of state, yet the latter is contained in the former as a limiting case. This canonical form of the equation of state enables us to give rigorous statistical mechanics representations for the van der Waals type parameters in it.

The virial equation of state[38] may be written as

$$\frac{\beta p}{\rho} = 1 - \frac{2\pi}{3}\beta \int_0^\infty dr\, r^3 V'(r)g(r,\rho,\beta) \qquad (17)$$

where r is the intermolecular separation, $g(r,\rho,\beta)$ is the equilibrium pair correlation function, and $V'(r)$ is the first derivative with respect to r of the pair potential. We consider a potential consisting of a repulsive and an attractive branch

$$V(r) = u_r(r) \quad \text{for } r \le \sigma$$
$$= u_a(r) \quad \text{for } \sigma < r \qquad (18)$$

where σ is the contact diameter and $u_r(r)$ and $u_a(r)$ are suitable functions of r representing the repulsive and the attractive potentials, respectively. For this potential model, the integral of eq 17 may be split into two parts

$$\frac{\beta p}{\rho} = 1 - \frac{2\pi\beta}{3} \int_0^\sigma dr\, r^3 u_r'(r)g(r,\rho,\beta) - $$
$$\frac{2\pi\beta}{3} \int_\sigma^\infty dr\, r^3 u_a'(r)g(r,\rho,\beta) \quad (19)$$

With parameters A and B defined by the formulas

$$A(\rho,T) = \frac{2\pi\beta}{3} \int_\sigma^\infty dr\, r^3 u_a'(r)g(r,\rho,\beta) \qquad (20)$$

$$B(\rho,T) = \frac{-\dfrac{2\pi\beta}{3} \int_0^\sigma dr\, r^3 u_r'(r)g(r,\rho,\beta)}{1 - \dfrac{2\pi\beta}{3}\rho \int_0^\sigma dr\, r^3 u_r'(r)g(r,\rho,\beta)} \qquad (21)$$

the virial equation of state (eq 19) can be cast into the form resembling the van der Waals equation of state

$$(p + A\rho^2)(1 - B\rho) = \rho\beta^{-1} \qquad (22)$$

This is called the generic van der Waals (GvdW) equation of state, which may be regarded as the canonical form of equation of state for fluids obeying an intermolecular potential of interaction that has a repulsive and an attractive branch. As shown in a previous paper,[20] the van der Waals equation of state is the limiting case of the eq 22 that arises as $\rho \rightarrow 0$ and $T \rightarrow \infty$, because $A \rightarrow a'$ and $B \rightarrow b'$ in the aforementioned limits.

For a fluid consisting of polyatomic molecules made up of N interaction sites, the definitions of A and B are generalized to the forms

$$A(\rho,T) = \frac{1}{N^2} \sum_{i,j=1}^N A_{ij}(\rho,T) \qquad (23)$$

$$B(\rho,T) = \frac{1}{N^2} \sum_{i,j=1}^N B_{ij}(\rho,T)\left[1 + \frac{\rho}{N^2} \sum_{i,j=1}^N B_{ij}(\rho,T)\right]^{-1} \qquad (24)$$

where

$$A_{ij}(\rho,T) = \frac{2\pi\beta}{3} \int_{\sigma_{ij}}^\infty dr_{ij}\, r_{ij}^3 u'(r_{ij})g(r_{ij},\rho,\beta) \qquad (25)$$

$$B_{ij}(\rho,T) = -\frac{2\pi\beta}{3} \int_0^{\sigma_{ij}} dr_{ij}\, r_{ij}^3 u'(r_{ij})g(r_{ij},\rho,\beta) \qquad (26)$$

In these expressions, $g(r_{ij},\rho,\beta)$ is the pair correlation function between sites i and j in molecules. It should be noted that the triplet correlation function contributions that may appear in the virial form for the equation of state for polyatomic fluids are neglected in these formulas. They contribute a relatively small amount. Such contributions can be readily included in the definitions of A and B.

2.2. Modified Free Volume Theory and the Self-Diffusion Coefficient. The main idea of free volume theory is that voids (free volumes) are created by density fluctuations in liquids and diffusion occurs as molecules jump into such voids. A number of theories of diffusion have been developed based on this picture[23,24,39,40] in the past. Of particular interest to us here is the theory proposed by Cohen and Turnbull.[23] This theory has been modified by Eu and his collaborator[25-28] so as to make it useful for the practical calculation of diffusion coefficients of liquids, and for such modification the GvdW equation of state has played a crucial role in providing a statistical mechanical means to calculate the mean free volume accurately. In their

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modified free volume (MFV) theory of diffusion, the self-diffusion coefficient D is given in the form[25]

$$D = D_{HS}{}^{\circ} \exp(-\alpha v_0/v_f) \qquad (27)$$

where v_f is the mean free volume, v_0 is the critical free volume just large enough to allow a molecule to move into, α is an adjustable parameter, which provides a measure of free volume overlap and is approximately unity in value, and $D_{HS}{}^{\circ}$ is the hard sphere Chapman–Enskog self-diffusion coefficient,[34] which may be taken in the form

$$D_{HS}{}^{\circ} = \frac{3}{8\sigma^2\rho} \sqrt{\frac{k_B T}{\pi m}} \qquad (28)$$

The important quantity that must be precisely given in the expression for D in eq 27 is the mean free volume v_f, but it has not been given a rigorous treatment by means of statistical mechanics in the existing free volume theories[24,40,41] other than the MFV theory of diffusion mentioned. In the MFV theory, since the parameter B is a statistical mechanical measure of mean excluded volume according to the GvdW equation of state, the mean free volume can be defined by

$$v_f = v(1 - B\rho) \quad v = 1/\rho \qquad (29)$$

It thus acquires a precise statistical mechanical representation, because B is given by the statistical mechanical expression eq 21 or eq 24. Therefore, apart from the meaning of αv_0, the self-diffusion coefficient D in eq 27 is calculable by means of statistical mechanics in which we have some well-developed methods of calculating the equilibrium pair correlation functions involved, for example, integral equation theories[38,42–44] or computer simulation methods.[45]

In the present work, the minimum free volume for diffusion v_0 is interpreted as a mean molecular volume. It is estimated by employing the van der Waals volume reported in the literature. Edward[46] reports it to be 0.0342 nm^3 for carbon dioxide at $T = 236$ K. Since it varies with temperature, we take 0.0363 nm^3 for it at all temperatures, which is approximately the intermediate value of the possible range for the effective molecular size of carbon dioxide in the literature. With this choice for v_0, there only remains the task of calculating the mean free volume by means of statistical mechanics on the basis of the intermolecular forces.

By application of eqs 27, 28, and 29, it now is possible to calculate the self-diffusion coefficient of the liquid at any thermodynamic state, provided that $g(r,\rho,\beta)$ is known. In a previous study on argon and methane in this series,[29] we have used a Monte Carlo (MC) simulation method to calculate the pair correlation function and therewith the self-diffusion coefficients of argon and methane. In the present work, which is a polyatomic generalization of the aforementioned work, MC simulations are also used to calculate the site–site pair correlation functions for carbon dioxide. In this work, the parameter B is computed with eq 24.

2.3. Monte Carlo Simulations. The pair correlation function $g(r,\rho,\beta)$, which is required for the self-diffusion coefficient in eq 27 and the shear viscosity in eq 15, has been computed by employing an MC simulation method, which allows us to calculate the site–site pair correlation functions. A standard Metropolis algorithm[45] was used to simulate the liquid carbon dioxide in constant particle number N, volume V, and temperature T conditions. The simulations were performed by using the Lennard-Jones two-site-interaction potential model with the

parameters employed by Singer et al.,[47] $\epsilon/k_B = 163.6$ K, $\sigma = 0.299$ nm, and $b = 0.237$ nm, where b is the molecular elongation (i.e., the distance between the centers of the sites). The Lennard-Jones parameters for the molecular carbon dioxide in the spherical molecule approximation was taken from literature[48] as $\epsilon/k_B = 251.2$ K and $\sigma = 0.375$ nm. A total number of 250 molecules were distributed inside a cubic simulation cell with standard periodic boundary conditions and in the minimum image convention. To equilibrate the system, 10 000 Monte Carlo cycles were performed, and then another 10 000 cycles were carried out to collect the ensemble averages. Thermodynamic equilibrium conditions were fulfilled by performing two different trial moves, random displacement of the center of mass and random rotation around the center of mass of the molecules. Each simulation cycle consists of 150 displacement trial moves and 150 rotational moves. The potential cutoff distance was set to half of the box length.

3. Comparison with Experiment

There are two quantities to compare with experiment in the present theory. One is the self-diffusion coefficients, given by eq 27, of carbon dioxide at various temperatures and densities, and the other is the viscosity computed by means of eq 15 with the self-diffusion coefficients calculated with eq 27 as a molecular theory input. It should be noted that if the parameter $v^* \equiv \alpha v_0$ is estimated as described earlier, then the theory for η becomes an ab initio molecular theory in the supercritical region, but in the subcritical regime, it becomes a semiempirical theory owing to the cutoff parameter ξ associated with the density fluctuation range, which is usually less than r_{max}. (Upon calculation of an average with $P(\xi)$, this parameter is replaced by ζ.) Nevertheless, once the parameter is fixed at a temperature for a given liquid, the theory for the shear viscosity gives correct predictions of the density and temperature dependence of transport coefficients of liquids at all other temperatures on the basis of intermolecular forces alone. The theory is found to remain reliable over the density and temperature ranges experimentally explored so far.

3.1. Self-Diffusion Coefficient of Carbon Dioxide. The self-diffusion coefficients have been calculated as described earlier for carbon dioxide. The results are compared with experimental data by Etesse et al.[1] in Figure 1, where the self-diffusion coefficients at various temperatures are plotted against density. The meanings of the symbols in Figure 1 are as follows: ◇ (experiment), ● (theory) at $T = 348.15$ K; △ (experiment), ∗ (theory) at $T = 323.15$ K; □ (experiment), × (theory) at $T = 298.15$ K; ○ (experiment), + (theory) at $T = 273.15$ K. The critical parameters of carbon dioxide are $p_c = 7.38$ MPa, $T_c = 304.2$ K, and $\rho_c = 0.466$ g cm^{-3}. Therefore, the isotherms ◇, ● and △, ∗ are supercritical whereas the isotherms □, × and ○, + are subcritical. We have set $\alpha = 1$ for all temperatures and then have estimated the critical free volume v_0 with the diameter of the sphere given by

$$r_0 = \frac{2^{1/6}\sigma}{\left(1 + \sqrt{1 + \frac{3T^*}{2}}\right)^{1/6}} \qquad (30)$$

where σ is the diameter of the van der Waals sphere estimated for carbon dioxide. This result is obtained by calculating the classical turning point of a head-on collision for the Lennard-Jones potential at temperature T under the assumption that σ of the van der Waals sphere is a Lennard-Jones potential parameter
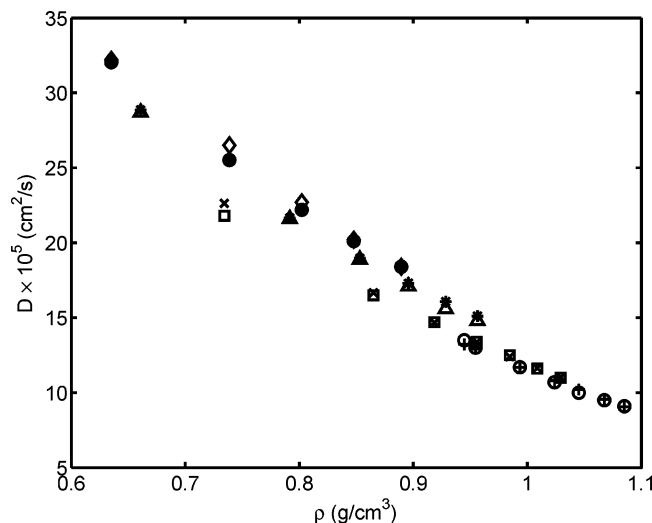
Figure 1. Theoretical density dependence of D for carbon dioxide compared with experimental data[1] at various temperatures. The meanings of the symbols are: $\diamond$ (experiment), $\bullet$ (theory) at $T = 348.15$ K; $\triangle$ (experiment), $*$ (theory) at $T = 323.15$ K; $\square$ (experiment), $\times$ (theory) at $T = 298.15$ K; $\circ$ (experiment), $+$ (theory) at $T = 273.15$ K.

for carbon dioxide at $T = 0$. With r_0 thus estimated, we obtain v_0 for carbon dioxide in the form

$$v_0 = \frac{\sqrt{2}}{\left(1 + \sqrt{1 + \frac{3T^*}{2}}\right)^{1/2}} \, v_E \tag{31}$$

where $v_E = \pi\sigma^3/6$ is the van der Waals volume of carbon dioxide estimated according to the Edward rule.[46] By using this critical free volume, we have computed the self-diffusion coefficients for supercritical carbon dioxide with eq 27 for which the mean free volume v_f given by eq 29 is calculated with the pair correlation function obtained by the MC simulations described earlier. For subcritical carbon dioxide, v_E is used for the critical free volume throughout the subcritical temperature range. It should be noted that since by simply setting $\alpha = 1$ the adjustable parameter is disposed of for all temperatures and densities the theory for D becomes free from the necessity of adjusting its value any further.

The choice of v_0 described earlier needs an explanation. Since the MC simulations for $g(r)$, we have employed a two-site model for carbon dioxide whereas for the critical free volume v_0 we have a spherical model for the molecule. These appear to be inconsistent with each other. However, it must be recognized that the van der Waals radius for carbon dioxide has been estimated by the Edward rule, which takes into account the molecular structure. Therefore, the nonspherical or the two-site nature of the molecule has been indirectly taken into account to estimate the critical free volume. Whether details of the molecular structure are taken into account in estimating v_0 or not, the end result is just a number, and it does not matter whether a spherical or nonspherical model is used for estimation of v_0 as long as the esimation is reasonable in magnitude.

With the critical free volume thus estimated, the density dependence of D is found to be very good for all temperatures considered, both supercritical and subcritical. There are slight deviations from experimental values in the low-density end of the range for which the experimental values are reported. These results indicate that the minimum (critical) volume for activating diffusion is the molecular volume given by the van der Waals diameter, which has been estimated from the thermodynamic data by the Edward rule.[46]
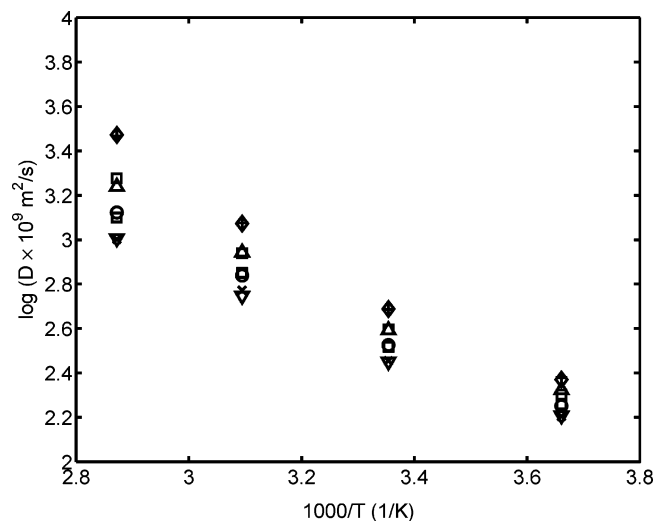

Figure 2. Theoretical temperature dependence of D for carbon dioxide compared with experimental data along various isobars. The meanings of the symbols are: $\diamond$ (experiment), $+$ (theory) at $p = 20.89$ MPa; $\square$ (experiment), $\triangle$ (experiment), $\triangle$ (theory) at $p = 27.03$ MPa; $\circ$ (experiment), $\times$ (theory) at $p = 34.61$ MPa; $\triangledown$ (experiment), $+$ (theory) at $p = 41.51$ MPa.

In Figure 2, the temperature dependence of D is compared with experimental values for carbon dioxide along various isobars. The symbols are defined as follows: $\diamond$ (experiment), $+$ (theory) at $p = 20.89$ MPa; $\square$ (experiment), $\triangle$ (theory) at $p = 27.03$ MPa; $\circ$ (experiment), $\times$ (theory) at $p = 34.61$ MPa; $\triangledown$ (experiment), $+$ (theory) at $p = 41.51$ MPa. It is again found that agreement with experiment is excellent for all isobars considered. Evidently, the temperature dependence of D is not of an Arrhenius type since log D versus T^{-1} is not linear. Nevertheless, it should be noted that the formula for D in eq 27 may be cast into a form reminiscent of the Arrhenius activation energy form

$$D = D_{HS}° \exp\left(-\frac{\alpha v_0 p_{eff}}{k_B T}\right) \tag{32}$$

where

$$p_{eff} = (p + A\rho^2) \tag{33}$$

We have used the generic van der Waals equation of state (eq 22) to obtain the form for D in eq 32 from eq 27. It is possible to interpret $\alpha v_0 p_{eff}$ as the work required to create a cavity of size αv_0 in the liquid, such that diffusion is facilitated. Therefore, $\alpha v_0 p_{eff}$ is akin to the activation energy in the Arrhenius activation theory of diffusion, but it depends on temperature, as is evident from Figure 2. Having successfully validated the MFV theory formula for D, we are now ready to apply it to calculate the shear viscosity of carbon dioxide in both gas and liquid density regimes.

3.2. Shear Viscosity of Carbon Dioxide. With the self-diffusion coefficients successfully calculated for carbon dioxide at various temperatures and densities, it is now possible to calculate the shear viscosity of carbon dioxide by employing the viscosity formula (eq 15). The kinetic part η_k of the shear viscosity is smaller than the potential part η_v by an order of magnitude or more in the liquid density regime. It therefore does not play an important role in determining the density and temperature dependence of the shear viscosity in the liquid density regime. In fact, it is possible to simply use the empirical shear viscosity of gas. But we find that it can be calculated to a good approximation by using the Enskog theory formula[49]
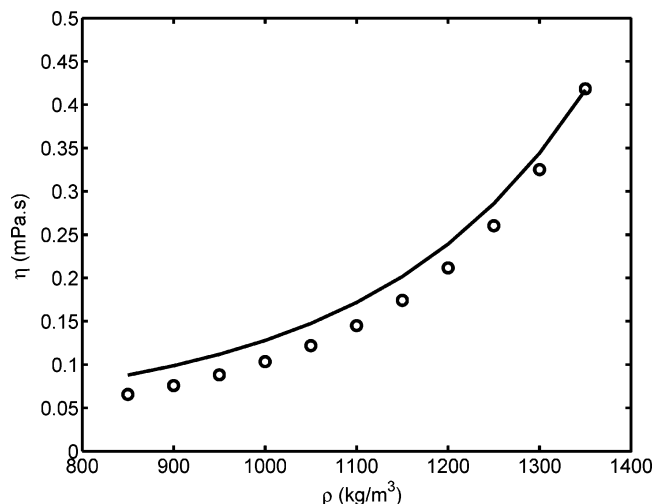
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Figure 3. Shear viscosity vs density for carbon dioxide at $T = 323$ K. The solid curve is the experimental data according to the fitting formula proposed by Fenghour et al.,[9] and the open circles are the theoretical predictions by the present theory.

Figure 4. Shear viscosity vs density for carbon dioxide at $T = 240$ K. The theoretical shear viscosity is calculated in two ways, one ($\diamond$) without the cutoff parameter ξ, namely, $\xi \geq r_{max}$, and the other (open circles) with $\zeta = 4.70 - 8.51\rho + 3.86\rho^2$. The solid curve is experimental data by Fenghour et al.[9]

since the anisotropic part makes a rather minor contribution and the liquid shear viscosity is little affected thereby. Otherwise, one has to invest a large amount of time and effort to compute the minor contribution that the anisotropic part makes.

Since in the supercritical regime the density fluctuation range is known to be equal to or larger than the range r_{max} of the interaction potential, the parameter ζ is equal to zero. Consequently, the shear viscosity formula is free from an adjustable parameter and can be predicted if only the potential energy parameters are given. In Figure 3, the shear viscosity at $T = 323$ K (a supercritical temperature) predicted by the present theory is compared with the experimental data. In Figure 3, the solid curve is the empirical fitting formula representing the experimental data, which is reported by Fenghour, Wakeham, and Vesovic,[9] and the open circles (O) are theoretical results computed with eqs 7–9 with $\xi \geq r_{max}$. Therefore, in this case, the viscosity formula is free from the cutoff parameter ξ and can be calculated if the potential parameters are known. The density dependence of the predicted shear viscosity is qualitatively correct compared with experiment, although the theoretical values are consistently lower than the experimental values for almost all density values. A possible source of deviation from experiment may be attributed to the MC simulations, which are known to be relatively poor in the gaseous density regime. This attribution of possible numerical errors to the MC simulations becomes plausible if we examine the shear viscosity in the subcritical regime, for example, $T = 240$ K at which the liquid is sufficiently far from the critical temperature, so that the critical density fluctuations causing numerical errors in the MC simulations are absent.

In Figure 4, we compare the shear viscosity of the present theory with the experimental data at $T = 240$ K. The theoretical shear viscosity is calculated in two ways. One is computed with eq 8 with $\omega(\rho,T)$ given by eq 9 for which $\xi \geq r_{max}$ as for Figure 3. These results therefore are also free from the cutoff parameter ξ. The values of η thus calculated are denoted by open diamonds ($\diamond$). The aim of this calculation is to assess the effect of not taking the average over the distribution of ξ. This was the method used in the previous work on the viscosity of carbon dioxide.[16] The other method of calculation used for η is to use eq 15 with $\zeta = a + b\rho + c\rho^2$, where $a = 4.70$, $b = -8.51$, and $c = 3.86$ in appropriate units. The results are denoted by open circles (O). The experimental data are reproduced by using
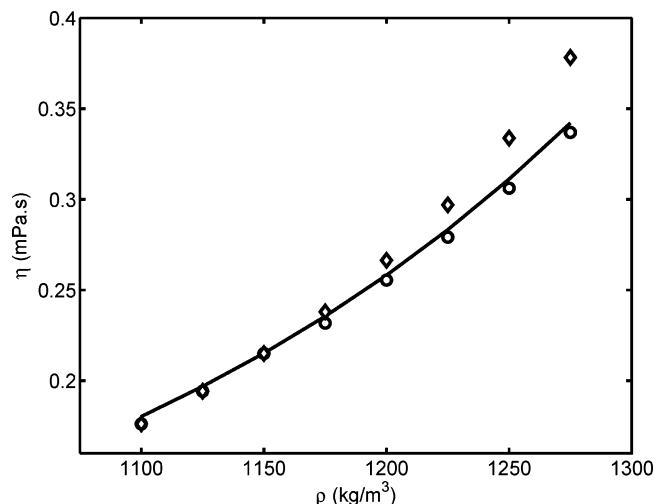
the fitting formula reported by Fenghour et al.[9] and denoted by the solid curve. The density dependence of η calculated with $\xi \geq r_{max}$ still yields a qualitatively correct behavior over the whole density range examined, but its deviation from the experimental value becomes noticeable as the density increases toward the high end. It should be emphasized here that the same expression taken for ζ will be used throughout the subcritical temperature region for carbon dioxide. Therefore, once ζ is determined at a temperature, for example, at $T = 240$ K as in the present case, the shear viscosity formula, eq 15, becomes predictive of η for all densities and all other temperatures with no further need for adjustment of the parameters, as will be shown presently. Thus, we have now acquired a robust molecular theory formula, which enables us to calculate the shear viscosity of carbon dioxide on the basis of the interaction potential model only.

To assess the utility of the viscosity formula with $\zeta = 4.70 - 8.51\rho + 3.86\rho^2$ for other subcritical temperatures, we have computed the shear viscosities of carbon dioxide over the liquid density ranges at $T = 250, 260, 280$, and 290 K in the subcritical temperature regime. The results are compared with experimental data reported by Fenghour et al.[9] in Figures 5 and 6. It should be noted that the theoretical values now have become predictive since the same form for ζ has been used as that for $T = 240$ K and there is no need to adjust it as the temperature is varied. The open circles (O) in Figures 5 and 6 are the theoretical results computed with eq 15, and the solid curves are the experimental data computed with the empirical fitting formula reported by Fenghour et al. The upper sets in Figures 5 and 6 are, respectively, for $T = 260$ K and $T = 250$ K whereas the lower sets are, respectively, for $T = 290$ K and $T = 280$ K. The theory is evidently in excellent agreement with the experiment.

The theoretical results computed with the aforementioned ζ are tantamount to ab initio values for the shear viscosity at the temperatures indicated, because the form for ζ is applicable to all other temperatures than $T = 240$ K, as mentioned earlier and thus fixed for carbon dioxide. In this sense, the parameter ζ seems to reflect an inherent feature of the liquid that is universal almost independent of T in the subcritical region. It may have a close relation to the void distribution in the subcritical domain of the liquid. In any event, the viscosity formula with ζ parametrized as suggested in this work is as good as the Fenghour–Wakeham–Vesovic fitting formula.
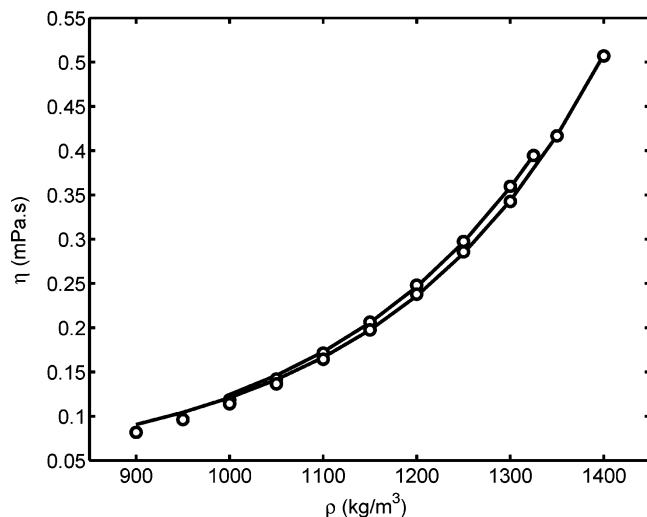
Figure 5. Shear viscosity vs density for carbon dioxide at $T = 260$ K and $T = 290$ K. The solid curves are experimental,[9] and the open circles (○) are theoretical. The upper curve is for $T = 260$ K whereas the lower curve is for $T = 290$ K.
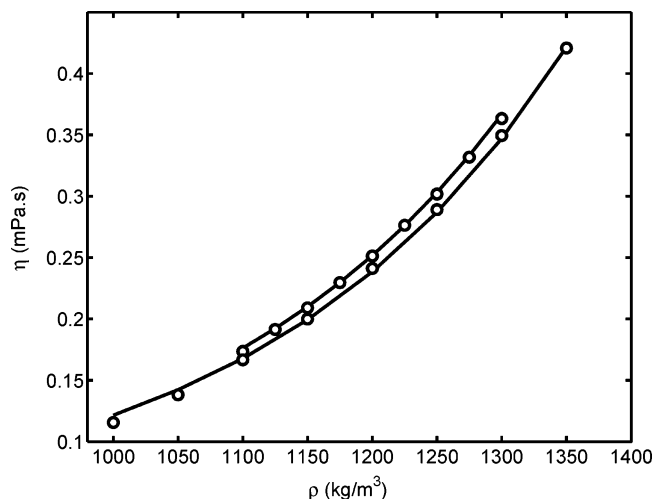

Figure 7. Temperature dependence of the shear viscosity of carbon dioxide at various isobars. The upper curve is at $\rho = 1.20$ g cm^{-3}; the middle curve is at $\rho = 1.25$ g cm^{-3}; the lower curve is at $\rho = 1.30$ g cm^{-3}. The solid curves are experimental, and the symbols are theoretical.

4. Concluding Remarks

In this paper, we have applied the density fluctuation theory of transport coefficients[14−18] to carbon dioxide and computed the shear viscosity of carbon dioxide without using empirical data on self-diffusion coefficients, and it removes the empirical approach taken in the papers by Rah and Eu. In this work, we have calculated the self-diffusion coefficients by means of the modified free volume theory, [25−28,50,51] which, with the help of the GvdW equation of state,[20−22] facilitates computation of the self-diffusion coefficients by means of an MC simulation method. Thus, the density fluctuation theory of shear viscosity has been made molecular although the critical free volume v_0 (with $\alpha = 1$) and ζ still remain to be fixed, and we have shown that the SE-like relation between the self-diffusion coefficient and shear viscosity in the liquid regime of density not only can be indeed made a molecular theory formula for shear viscosity but also is shown to be accurate and robust over wide ranges of density and temperature experimentally explored. The parameter v_0 can be reasonably well estimated on physical grounds, and ζ needs to be fixed only in the subcrital regime but only once at a temperature. The shear viscosity formula that we have tested in this work can be not only applied to further analyze experimental data on carbon dioxide but also used for various fluid dynamic investigations of flow properties of the liquid, which has a wide range of practical applications in chemistry and engineering. The present theory of viscosity, with only three parameters for ζ, may be said to provide, at least, a molecular theory alternative to the Fenghour−Wakeham−Vesovic fitting formula[9] employed for summarizing experimental data on the liquid viscosity.

Apart from such applications of the present theoretical results, the shear viscosity formula presented in this work is also significant in elucidating the molecular theory mechanism for transport processes and its relation to the structure of the liquid of interest from the statistical mechanical viewpoint. The present theory points to the importance of the role of voids in transport processes in liquids and diffusion processes in setting the time and spatial scales for transport processes of momentum and energy. The SE-like relation between the shear viscosity and self-diffusion coefficient is a manifestation of such a role played by diffusion of particles in the liquid. It is also important to

Figure 6. Shear viscosity vs density for carbon dioxide at $T = 250$ K and $T = 280$ K. The solid curves are experimental,[9] and the open circles (○) are theoretical. The upper curve is for $T = 250$ K whereas the lower curve is for $T = 280$ K.

Therefore, the present theory of viscosity provides a molecular theory alternative to such a fitting formula.

Since the temperature dependence of η is of interest and useful for assessing the capability of the theory, we have also computed the temperature dependence of η as a function of T at various isochores: $\rho = 1.20$ g cm^{-3}, 1.25 g cm^{-3}, and 1.30 g cm^{-3}. For this calculation, the form for ζ in the subcritical temperature region is the same as that already mentioned for the case of $T = 240$ K. The results are plotted and compared with experimental values in Figure 7. The symbols in Figure 7 are theoretical results whereas the solid curves are experimental data reproduced with the fitting formula of Fenghour et al.[9] The meanings of the symbols are as follows: open circles (○) for $\rho = 1.20$ g cm^{-3}; open squares (□) for $\rho = 1.25$ g cm^{-3}; open diamonds (◇) for $\rho = 1.30$ g cm^{-3}. Agreement with experiment is found to be very good. The behavior of η with regard to T is evidently not quite of the Arrhenius type.

We remark that all of the density values taken for the isochores in Figure 7 are larger than those along the liquidus curve in the phase diagram.
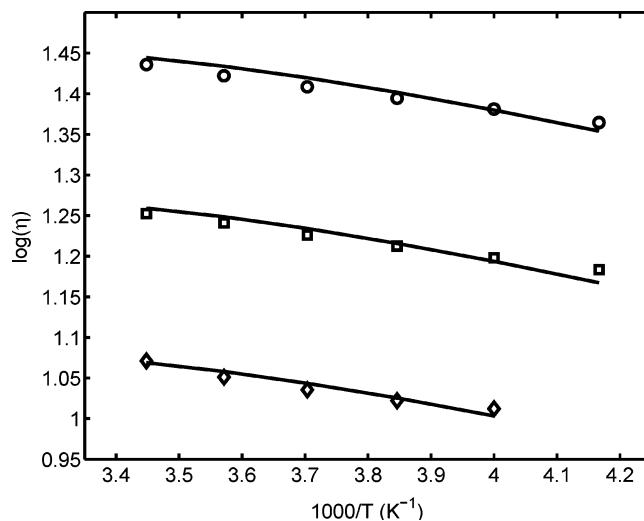
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recall that in the present theory the transport coefficients (e.g., viscosity and self-diffusion coefficients), which are nonequilibrium dynamical quantities, are now computable in terms of only the equilibrium pair correlation function and the equation of state, apart from the intermolecular forces, both of which closely reflect the structure of the liquid of interest. Therefore, dynamic quantities such as collision cross sections or Green's functions as in, for example, the linear response theory,[52,53] the Chapman–Enskog line of kinetic theory,[54] or the mode coupling theory do not enter into the potential energy contribution part of the shear viscosity.[55–57] Consequently, from the computational standpoint the present density fluctuation theory formula for shear viscosity and the concomitant self-diffusion coefficient are rather easily computable by means of relatively minor computational resources readily available at present. This is an important advantage of the density fluctuation theory results for transport coefficients presented in this work. It is, probably, helpful to note that the aforementioned alternative theories[52–57] have not so far yielded the density and temperature dependences of transport coefficients to the extent presented in this work.

On the basis of the body of numerical results compared with experimental data on the self-diffusion coefficients and shear viscosity of carbon dioxide in the liquid and high-density supercritical regime, it is possible to state that both the self-diffusion coefficient formula and the shear viscosity formula presented in this work are satisfactorily validated, and we are now in possession of a robust, at least semiempirical, molecular theory of transport coefficients of carbon dioxide and, probably, by extension, of other rigid linear molecules.

Supporting Information Available: Transport properties of carbon dioxide, including self-diffusion and shear viscosity parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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