

Pair Correlation Functions and the Self-Diffusion Coefficient of Lennard-Jones Liquid in the Modified Free Volume Theory of Diffusion[†]

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In this paper, we apply the Matteoli–Mansoori empirical formula for the pair correlation function of simple fluids obeying the Lennard-Jones potential to calculate reduced self-diffusion coefficients on the basis of the modified free volume theory. The self-diffusion coefficient thus computed as functions of temperature and density is compared with the molecular dynamics simulation data and the self-diffusion coefficient obtained by the modified free volume theory implemented with the Monte Carlo simulation method for the pair correlation function. We show that the Matteoli–Mansoori empirical formula yields sufficiently accurate self-diffusion coefficients in the supercritical regime, provided that the minimum free volume activating diffusion is estimated with the classical turning point of binary collision at the mean relative kinetic energy $3k_B T/2$, where k_B is the Boltzmann constant and T is the temperature. In the subcritical regime, the empirical formula yields qualitatively correct, but lower values for the self-diffusion coefficients compared with computer simulation values and those from the modified free volume theory implemented with the Monte Carlo simulations for the pair correlation function. However, with a slightly modified critical free volume, the results can be made quite acceptable.

1. Introduction

In the study of transport processes and other dynamical thermophysical properties of liquids, self-diffusion coefficients are important because self-diffusion of particles sets the basic time and spatial scales of dynamic evolution of the system and the viscosity and thermal conductivity may be expressed in terms of the self-diffusion coefficient. However, the molecular theoretic calculation of the self-diffusion coefficients of gases and liquids is not only difficult and laborious but also time consuming, since to be sufficiently accurate their computation generally has to be carried out by means of computer simulation methods—typically, a molecular dynamics (MD) simulation method. In a recent series of papers on the modified free volume (MFV) theory and its applications,^{1–5} it has been shown that the desired self-diffusion coefficients of liquids can be calculated efficiently and accurately if the equilibrium pair correlation function required for the calculation of the mean free volume is computed by means of a Monte Carlo (MC) simulation method. Comparison with experiment of the self-diffusion coefficients thus computed shows that they behave correctly with regard to the density and temperature dependence over the entire ranges of density and temperature experimentally studied or by (MD) simulation methods. The self-diffusion coefficients obtained by the MFV theory method implemented with the MC simulations, although rather simple and substantially time saving compared to the time and labor required of the molecular dynamic simulation methods for them, still take a considerable amount of numerical work to achieve the desired results with sufficiently good accuracy. Therefore, it would be useful to have some time- and labor-saving schemes for the computation of the self-diffusion coefficients of liquids. To answer this question posed, we need a reliable and easily

available source of the pair correlation function over the desired ranges of temperature and density.

Some time ago, Matteoli and Mansoori⁶ proposed an empirical formula for the pair correlation function of simple liquids obeying the Lennard-Jones potential, which they obtained by systematically fitting Verlet's computer simulation data,⁷ and then tested the formula for its reliability. As far as we can see, it seems to be reliable and robust when applied to compute thermodynamic functions. In this paper, we report on an application of the Matteoli–Mansoori (MM) formula for the pair correlation function to calculate the self-diffusion coefficient of the Lennard-Jones liquid. The self-diffusion coefficient thus calculated is tested with respect to its density and temperature dependence in comparison with the self-diffusion coefficients computed by means of MD simulations and the MFV theory data obtained by means of MC simulations. We also show how the results can be made quite acceptable in practice if the minimum free volume activating diffusion is suitably chosen. Since self-diffusion coefficients can be related to other transport coefficients,^{1–5,8,9} the applicability of the MM formula to the calculation of reliable self-diffusion coefficients can have a considerable practical significance for other transport coefficients, such as viscosity and thermal conductivity, of liquids.

In section 2, the MM formula for the pair correlation function is presented in reduced units of variables. In section 3, the self-diffusion coefficient formula in the MFV theory of diffusion is presented together with a brief review of the generic van der Waals (GvdW) equation of state^{10–12}—the canonical equation of state—which plays a crucial role in the MFV theory of diffusion. In the MFV theory, the mean free volume contains an indispensable piece of molecular information on the fluid, and this information is provided by the canonical equation of state, which enables us to define the mean excluded volume in the most natural manner. The brief review of the canonical

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TABLE 1: Coefficients for Parameters

i	$q_{1,i}$	$q_{2,i}$	$q_{3,i}$
h'	403.5	-371.7	-1.552
m	22.79	-17.54	-0.0508
$g(d)$	1.708	-0.8569	0.8196
λ	0.5644	-0.3057	0.8579
ξ	0.2411	0.1387	4.216
β	5.289	-1.180	0.3996
θ	71.44	-46.68	1.100

equation of state therefore prepares the reader for the statistical mechanical representation of the mean free volume. Section 4 is for validation of the MM formula for the pair correlation function, where the self-diffusion coefficients are calculated with the MM formula and compared with the MD simulation results reported in the literature and the MFV theory self-diffusion coefficients calculated by means of a MC simulation method for the pair correlation function. Section 5 is for the conclusion.

2. The MM Formula for the Pair Correlation Function

In terms of the reduced distance, temperature, and density defined by

$$x = r/d, T^* = k_B T/\epsilon, \rho^* = \rho \sigma^3$$

where r is the radial distance, d is the contact distance, σ is the Lennard-Jones potential parameter scaling the distance, and ϵ is the potential well depth, the MM formula⁶ for the radial distribution function (i.e., pair correlation function) is given by

$$g(x) = 1 + x^{-m} [g(d) - 1 - \lambda] + \frac{(x - 1 + \lambda)}{x} \cos[\beta(x - 1)] \exp[-\xi(x - 1)] \quad (x \geq 1) \quad (1)$$

$$= g(d) \exp[-\theta(x - 1)^2] \quad (x < 1) \quad (2)$$

where $m \geq 1$, $h = d/\sigma$, λ , ξ , β , θ , and $g(d)$ are adjustable parameters and d denotes the contact distance. These parameters are expressed as functions of reduced temperature T^* and reduced number density ρ^* : for $p_i = \theta$, $g(d)$, λ , β , and $h' = 1000(h - 1)$

$$p_i = [q_{1,i} + q_{2,i} \exp(-1/T^*)] \exp(q_{3,i} \rho^*) \quad (3)$$

and for $p_i = m$ and ξ

$$p_i = [q_{1,i} + q_{2,i} \exp(-1/T^*)][q_{3,i} + \rho^{*2}]/\rho^* \quad (4)$$

With these choices for the coefficients, the radial distribution function satisfies the limiting behavior at $\rho \rightarrow 0$ and $x \rightarrow \infty$. Furthermore, it tends to the hard sphere radial distribution function $g^{hs}(x)$ as $T \rightarrow \infty$. The coefficients $q_{1,i}$, $q_{2,i}$, and $q_{3,i}$ are summarized in Table 1. The radial distribution function was shown to reproduce the known results for $g(x)$. We will apply this MM formula for $g(x)$ to calculate the self-diffusion coefficients of the Lennard-Jones liquid and test its utility in this work.

3. The Self-Diffusion Coefficient in the MFV Theory

According to the MFV theory of diffusion,¹⁻³ which is a modification of the Cohen-Turnbull (CT) free volume theory¹³ of diffusion, the self-diffusion coefficient of simple fluids is given by the formula

$$D = D_0 \exp(-\alpha v_0/v_f) \quad (5)$$

where α is a parameter associated with the overlap of free volumes, v_0 is the minimum free volume activating diffusion, and D_0 is the low density limit of D , which may be taken as the Chapman-Enskog self-diffusion coefficient for a hard sphere fluid¹⁴

$$D_0 = 1.019 \frac{3}{8\sigma^2 \rho} \sqrt{\frac{k_B T}{\pi m}} \quad (6)$$

In this formula, m is the reduced mass of the molecule. The parameter α is usually around unity but may be absorbed into v_0 . Then, αv_0 may be simply taken for a single parameter. In fact, it may be regarded as the molecular volume in the case of simple fluids or may be taken as the minimum free volume activating diffusion. In any case, diffusion is facilitated when a void of the size of molecular volume or the minimum free volume is created in the neighborhood of a particle in the fluid. With such a choice for αv_0 , there now remains the task of expressing the mean free volume v_f in terms of molecular quantities in order to compute the self-diffusion coefficient.

Historically, the mean free volume v_f has been an elusive quantity that has defied a rigorous statistical mechanical quantification. In fact, not only has the inaccurate form proposed for it by van der Waals saddled the original van der Waals equation of state with glaring defects in the subcritical regime, but also the absence of an accurate statistical mechanical representation of it has deprived various free volume theories,¹⁵⁻¹⁷ including the CT free volume theory, of their potential to become a molecular theory.

Fortunately, the canonical equation of state—the generic van der Waals equation of state¹⁰⁻¹²—captures the elusive mean free volume in terms of the pair correlation function and the intermolecular force to serve the MFV theory of diffusion. This mean free volume in the MFV theory of diffusion is calculated by means of the generic van der Waals (GvdW) parameter B appearing in the canonical equation of state

$$(p + A\rho^2)(1 - B\rho) = \rho k_B T \quad (7)$$

which, as $\rho \rightarrow 0$ and $T \rightarrow \infty$, reduces to the van der Waals equation of state

$$(p + a'\rho^2)(1 - b'\rho) = \rho k_B T \quad (8)$$

where a' and b' denote the van der Waals constants. To arrive at this form for the equation of state from the virial equation of state in statistical mechanics,

$$\frac{p}{\rho k_B T} = 1 - \frac{2\pi}{3k_B T} \int_0^\infty dr r^3 \frac{du}{dr} g(r, \rho, T) \quad (9)$$

we assume that the potential energy has a repulsive and an attractive branch

$$\begin{aligned} u(r) &= u_t(r) + u_a(r) \\ u(r) &= u_t(r)\theta(\sigma - r) \\ &= u_a(r)\theta(r - \sigma) \end{aligned} \quad (10)$$

with $\theta(x)$ denoting the Heaviside step function: $\theta(x) = 0$ for $x < 0$ and $\theta(x) = 1$ for $x > 0$. Then, if the GvdW parameters A

and B are defined by the statistical mechanical formulas,

$$A(\rho, T) = \frac{2\pi}{3k_B T} \int_0^\sigma dr r^3 \frac{du_a}{dr} g(r, \rho, T) \quad (11)$$

$$B(\rho, T) = - \frac{\frac{2\pi}{3k_B T} \int_0^\sigma dr r^3 \frac{du_r}{dr} g(r, \rho, T)}{1 - \frac{2\pi\rho}{3k_B T} \int_0^\sigma dr r^3 \frac{du_r}{dr} g(r, \rho, T)} \quad (12)$$

then it is easy to show that the virial equation of state can be written in the form of the canonical equation of state,¹⁰ as given in eq 7. It should be noted that eq 7 with definitions 11 and 12 is identical with the virial equation of state. Since the canonical equation of state 7 suggests that $B\rho$ is a measure of the mean excluded volume of the fluid, it is natural to define the mean free volume by

$$v_f = v(1 - B\rho) \quad (13)$$

Thus, with eq 12 for B , we now obtain the long desired statistical mechanical representation of mean free volume, which can be calculated if the intermolecular force is given. In this manner, apart from the factor αv_0 , the self-diffusion coefficient 5 is rendered molecular by virtue of eqs 12 and 13. The minimum free volume or the factor αv_0 is not possible to calculate by means of a molecular theory within the framework of the CT free volume theory of diffusion, but it is perhaps welcome to have a physically interpretable parameter $v^* \equiv \alpha v_0$. Since it may be interpreted as a critical free volume activating diffusion, it in fact gives a physically reasonable way to relate a mental picture of the liquid to how and what stage diffusion occurs in the liquid. Therefore, with a suitable choice for the parameter v^* in terms of molecular parameters, the MFV theory formula for diffusion becomes fully molecular. In this manner, the task of computing D for simple liquids is now reduced to the calculation of the equilibrium pair correlation function $g(r, \rho, T)$.

In the previous studies of the transport properties of liquids, $g(r, \rho, T)$ was computed by means of either integral equations^{18–22} or a Monte Carlo (MC) simulation method.^{4,5} In particular, the self-diffusion coefficients^{4,5} calculated by means of MC simulations were found to be rather accurate and robust with regard to their density and temperature dependence, when compared with experiment or molecular dynamics simulation results. The MC simulation approach for $g(r, \rho, T)$ is quite efficient and practicable with the readily available computational resources at present. Nevertheless, it would be useful if there were a procedure that could save time even further. Fortunately, there are some empirically determined formulas for $g(r, \rho, T)$ in the literature, which is reliable, albeit limited to some ranges of temperature and density. One example is the empirical formula proposed by Matteoli and Mansoori.⁶ We apply it to calculate D for the Lennard-Jones liquid.

4. Validation of the MM Formula

In this work, we examine the reliability of the MFV theory of diffusion for the Lennard-Jones fluid in comparison with the MD simulation results. Also, at the same time, we examine the utility of the MM formula for the pair correlation function to calculate the self-diffusion coefficient in comparison with both of the former ones. In other words, v_f is calculated by using

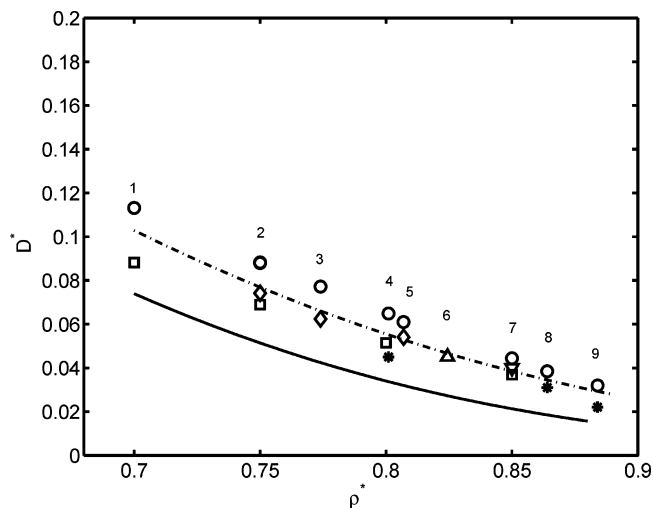


Figure 1. Comparison of D^* computed with the MM formula and D^* computed with $g(x)$ computed by an MC method and an MDS method. The solid curve is for D^* computed with the MM formula ($T^* = 0.80$), and the open circles (\circ) are for D^* computed with the MC simulations for $g(x)$, whereas the open squares (\square) are by Meier et al.;²⁷ the open triangles (\triangle) are by Levesque et al.;²⁸ the open inverted triangles (∇) are by Kuschick et al.;²⁹ the asterisks ($*$) are by Heyes;³⁰ and the open diamonds (\diamond) are by Carelli et al.,²⁶ all of which are the MDS data. $\rho^* = \rho\sigma^3$. The groups of data points denoted by the numerals are at the following temperatures: $T^* = 0.80$ for 1, 2, and 7; $T^* = 0.81$ for 8 and 9; $T^* = 0.82$ for 6; and $T^* = 0.83$ for 3 and 5. The dash-dot curve is the MM formula D^* computed with $v_0 = \pi(0.909\sigma)^3/6$.

eqs 1–4 in eq 12 for the pair correlation function. We then calculate therewith the reduced self-diffusion coefficient

$$D^* = \sqrt{m/\sigma^2} \epsilon D$$

Since the critical temperature for the Lennard-Jones fluid considered is reported^{23–25} to be about 1.30 in reduced units, we examine two isotherms $T^* = 1.35$ and $T^* = 1.80$ in the supercritical regime and isotherms at $T^* = 0.80$ – 0.83 in the subcritical regime to assess the utility of the MM formula. The choice of the isotherms are largely arbitrary except that it is dictated, to some extent, by the literature data to compare with.

In Figure 1, the self-diffusion coefficients calculated with the MM formula for $g(x)$ at $T^* = 0.80$ are compared with experimental data,²⁶ molecular dynamics simulation (MDS) results,^{27–30} and the MFV theory D^* computed with $g(x)$ obtained by means of an MC simulation method at various values of reduced density $\rho^* = \rho\sigma^3$; the same MC simulation method is used as described in ref 4. We have set $\alpha = 1$ and used $v_0 = \pi\sigma^3/6$, with the molecular volume in the case of D^* calculated by means of the MC simulation method. The solid curve is for D^* computed with the MM formula at $T^* = 0.80$, and other points are either MDS results or the MC simulation results of the MFV theory at various temperatures: $T^* = 0.80$ for groups 1, 2, and 7; $T^* = 0.81$ for groups 8 and 9; $T^* = 0.82$ for group 6; $T^* = 0.83$ for groups 3 and 5. The open circles (\circ) are for D^* of the MFV theory computed with the MC simulations for $g(x)$, whereas the open squares (\square) are by Meier et al.;²⁷ the open triangles (\triangle) are by Levesque et al.;²⁸ the open inverted triangles (∇) are by Kuschick et al.;²⁹ the asterisks ($*$) are by Heyes;³⁰ and the open diamonds (\diamond) are by Carelli et al.,²⁶ all of which are the MDS data. The MM formula gives the self-diffusion coefficients lower than the rest of the values listed earlier. We have found by experience that correct values of $g(x)$ in the immediate neighborhood of the contact distance are very

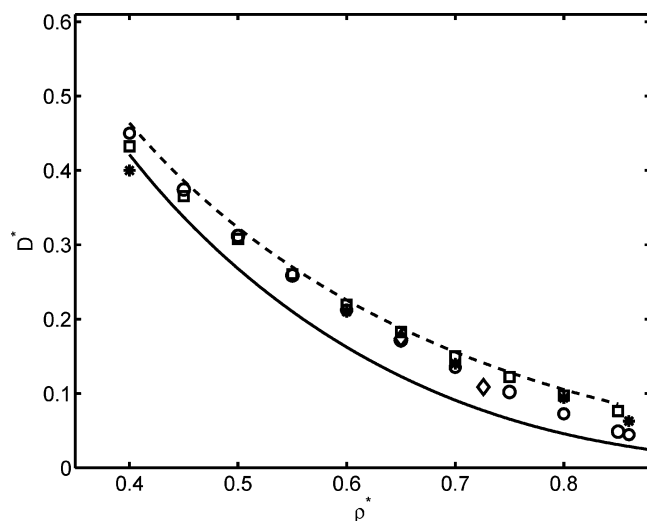


Figure 2. Comparison of D^* computed with the MM formula, D^* computed with $g(x)$ by MC simulations, and MDS data at various reduced densities ρ^* . The solid curve is for the MM formula for $g(x)$ at $T^* = 1.35$, and the open circles (O) are the MC simulation for $g(x)$ at $T^* = 1.35$, whereas other symbols are MDS data: open squares (\square) by Meier et al.²⁷ at $T^* = 1.35$; asterisks (*) by Heyes³⁰ at $T^* = 1.35$, and open diamonds (\diamond) by Carelli et al.²⁶ at $T^* = 1.39$. The broken curve represents D^* computed at $T^* = 1.35$ with the MM formula for $g(x)$ and the formula for v_0 given in eq 14.

important for the correct values of D^* . The probable cause for the lower values given by the MM formula seems to lie in its unsatisfactory fitting near the contact distance. This explanation seems to become more plausible, since if v_0 is calculated with σ altered to 0.909σ , which gives rise to a slightly larger value of the contact distance than the supercritical values, the self-diffusion coefficients calculated with the MM formula compare better with the simulation values over the whole density range considered. In this connection, it should be noted that v_0 is more closely related to the hard core part of the distribution function than to the attractive part, inasmuch as the molecular volume is concerned. The self-diffusion coefficient D^* calculated at $T^* = 0.80$ by using the MM formula with $v_0 = \pi(0.909\sigma)^3/6$ is represented by the dash-dot curve in Figure 1. The MM formula value for D^* is clearly improved compared with other data. However, the choice of 0.909σ for the diameter of the particle is arbitrary. This somewhat arbitrary procedure is not used for the MC simulation results (i.e., the open circles).

In Figure 2, we compare the self-diffusion coefficients computed similarly for those presented in Figure 1. The solid curve is for the MM formula for $g(x)$ at $T^* = 1.35$ and the open circles (O) are the MC simulation for $g(x)$ at $T^* = 1.35$, whereas other symbols are MDS data: open squares (\square) by Meier et al.²⁷ at $T^* = 1.35$; asterisks (*) by Heyes³⁰ at $T^* = 1.35$; and open diamonds (\diamond) by Carelli et al.²⁶ at $T^* = 1.39$.

Instead of using the molecular volume $\pi\sigma^3/6$ provided by the potential parameter σ , it may be estimated slightly differently. Since the apparent volume on contact of a pair of molecules should be dependent on temperature because at the classical turning point of a head-on collision between the molecules the potential energy must balance the mean kinetic energy $3k_B T/2$. By employing this device, we obtain the apparent molecular volume in the form

$$v_0 = \frac{\sqrt{2}}{(1 + \sqrt{1 + 3T^*/2})^{1/2}} \left(\frac{\pi\sigma^3}{6} \right) \quad (14)$$

Using this v_0 together with the MM formula to calculate B and

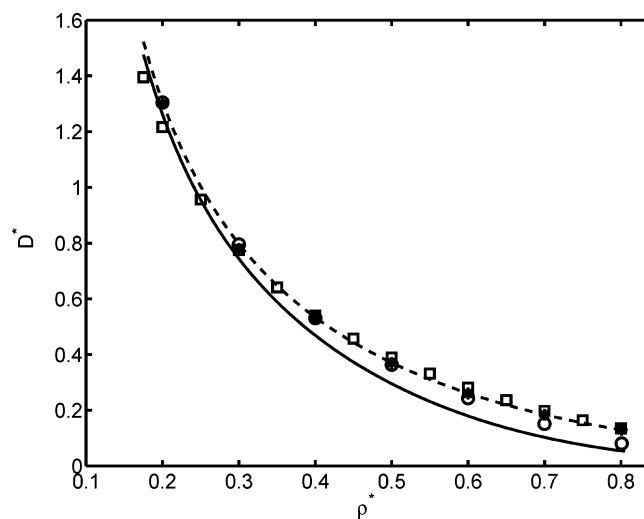


Figure 3. Comparison of D^* at $T^* = 1.80$ obtained with the MM formula, the MC simulation data, and MDS data for D^* . The meanings of the symbols and curves are the same as those for Figure 2.

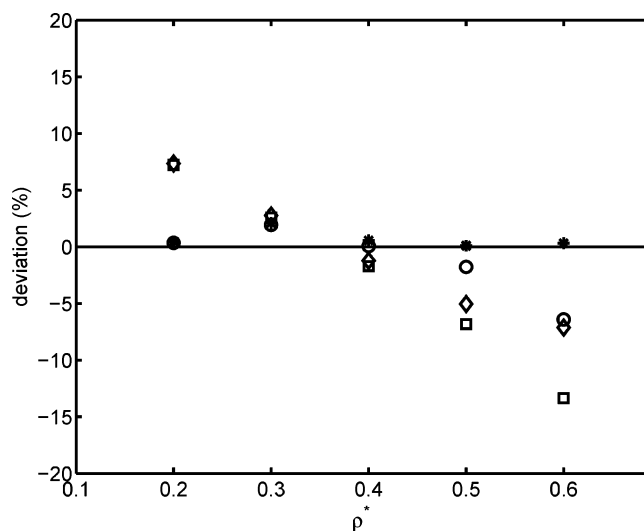


Figure 4. Percentage deviations plotted against ρ^* . Deviations of the MFV theory D^* by the MC simulation method and by the MM empirical formula from the MD simulation results of Heyes³⁰ and of Meier et al.²⁷

thus v_0 , we have computed D at $T^* = 1.35$. The broken curve in Figure 2 represents the self-diffusion coefficients thus computed, which evidently are in good agreement with other sets (i.e., the MDS data or the MC data) of D^* . It should be emphasized that v_0 given by eq 14 was not used for the open circles representing the values of D^* computed by the MFV theory with the MC simulation method for the pair correlation functions. The improvement thus gained for the MM formula results, in fact, suggests that there are some numerical errors in the fitting of the MM formula in the close neighborhood of the contact distance. Our experience shows that the values of $g(x)$ near $x = \sigma$ are very important for the accuracy of D^* .

In Figure 3, we have calculated the D^* values at $T^* = 1.80$ and compared them with MDS and MC simulation data. The meanings of the symbols and the curves are the same as for Figure 2. Again, we see that the MM formula with v_0 given by eq 14 yields D^* in good accuracy in comparison with the MC simulation data and other MDS data. To better show the relative merits of the two MFV theory data presented in Figure 3, we have plotted against ρ^* in Figure 4 the percentage deviations of the self-diffusion coefficients calculated by using the MFV

theory with the pair correlation functions obtained by the MC simulation method (\circ , \square) and the MM empirical formula ($*$, \diamond) from the MD simulation results of Heyes³⁰ and Meier et al.²⁷ The meanings of the symbols in Figure 4 are as follows: the MFV theory results by the MC simulation method relative to Heyes' MD simulation results are denoted by the open circles (\circ), and those relative to the MD simulation results of Meier et al. are denoted by open squares (\square), whereas the MFV theory results by the MM empirical formula relative to Heyes' MD simulation results are denoted by the asterisks ($*$), and those by the MM empirical formula relative to the MD simulation results of Meier et al. are denoted by the open diamonds (\diamond). We find that, compared with the results of Meier et al., both methods, the MC and MM formula results, deviate from the MD simulation results in the low and high density regimes, whereas they do so less compared with the Heyes MD simulation results.

On the basis of the comparison made in the figures presented earlier, it is now possible to state that it is trivial in time and effort to calculate a reasonably accurate and well behaved D^* value by means of the MM formula. There lies its utility for many practical problems requiring self-diffusion coefficients in the fields of chemistry, physics, and biology, and application of the MFV theory of diffusion is thereby made rather simple and straightforward. With the MM formula, it is now rather easy to compute the density and temperature dependence of viscosity and thermal conductivity of the liquid because they are related to the self-diffusion coefficient.^{8,9}

5. Conclusion

In this paper, we have shown that the MM formula for the equilibrium pair correlation function for the Lennard-Jones fluid can be fruitfully utilized to calculate the self-diffusion coefficient as a function of temperature and density to a good and reliable accuracy. Especially, in the supercritical regime, the MM formula can deliver the self-diffusion coefficients in reasonable accuracy, if the minimum free volume activating diffusion v_0 is chosen with the molecular volume given in eq 14. With such an empirical formula for $g(x)$ as the MM formula, it is now

possible to compute the self-diffusion coefficients of simple fluids rather easily in serviceable accuracy, which are ubiquitously applied in the study of numerous thermophysical, transport, and biological phenomena.

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