

Calculation of the transport properties of dense fluids using modified Enskog theory and an appropriate equation of state

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Received 18 July 2006; received in revised form 14 November 2006; accepted 3 February 2007

Available online 12 February 2007

Abstract

In this work, a new method based on the modified Enskog theory (MET) is presented for calculation of transport properties at high densities ($\rho > \rho_c$). The main limitation of using the MET is lack of experimental data for co-volume, b_0 . We have substituted b_0 from hard sphere (HS) theory and zero density transport properties from the kinetic theory of gases for HS in the MET expression, because of the fact that dense fluids behave more and less like a HS fluid. As a result, a simple linear expression for the self diffusion (D) and quadratic expressions for viscosity (η) and thermal conductivity (λ) coefficients have been obtained in terms of Y at high densities ($\rho > \rho_c$), where $Y = (T(\partial p/\partial T)_\rho)/\rho RT - 1$. To evaluate the obtained expressions, we have used experimental values of densities and the transport properties and calculated Y from the reported accurate equation of state (EOS) for argon and xenon. We have noticed that the quadratic fits for viscosity and thermal conductivity and the linear fit (when $T < T_c$) for self diffusion hold quiet well with the correlation coefficient, $R^2 \geq 0.9994$, when $\rho > \rho_c$. Also, we have found that the curves for different isotherms of a fluid fall onto a common curve at high densities over entire temperature range for which experimental data exist, but the curves depend on the nature of fluid. So, by using experimental data of transport properties for one isotherm and an accurate EOS for calculation of Y for a dense fluid, we may calculate the corresponding property of that fluid for any other isotherm. In this work, we have used this approach to predict the viscosity coefficient of n -alkanes from propane to n -octane and cyclohexane at different densities ($\rho > \rho_c$) and temperatures. To do such predictions, we need an accurate EOS for each compound which is not generally available. For this reason, we have made use of the modified linear isotherm regularity (MLIR). Therefore, using the calculated values of density and thermal pressure coefficient from the MLIR and the coefficients of the viscosity expression for each of these fluids, their viscosities have been predicted with the average percentage error less than 1.6%. To make the approach more general, we have used the principle of corresponding states to present viscosity expression independent of fluid in terms of the reduced variables. Therefore, one may use experimental data for one isotherm of an arbitrary fluid to find the coefficients of the reduced viscosity expression. Then, these coefficients may be used for other fluids at the same reduced temperature, T_r , to calculate the reduced viscosity. Here, we have selected n -butane as a reference compound because of abundance of experimental data. We have used the coefficients of the expression for n -butane and density and Y have been calculated from the MLIR, this approach gives viscosity of hydrocarbons with the average percentage error less than 1.7%. Similar approach has been used to calculate the self diffusion coefficient and thermal conductivity of dense fluids.

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Keywords: Modified linear isotherm regularity; Modified Enskog theory; Thermal pressure coefficient; Principle of corresponding states; Group contribution method

1. Introduction

Liquid viscosity is one of the most significant transport properties required by chemical engineers involved in reactor applications and heat and mass transfers. Accurate experimental measurements of viscosity are a complex task. Therefore, in this situation, any generalized prediction approach is highly

desirable for practical engineering uses. Reid et al. has reviewed many different viscosity methods [1]. The viscosity models found in literature range from highly theoretical to simple empirical correlations. The kinetic theory of dilute gases and the Chapman–Enskog theory [2] have formed accurate semi-theoretical models for the viscosity prediction of dilute gases. The Rainwater-Friend theory is used for prediction of viscosity in intermediate density range [3]. Also, the Rainwater-Friend theory was used for densities up to 2 mol/dm^{-3} by Najafi et al. [4]. Nevertheless, because of the complexity of the intermolecular forces in dense fluids, makes even a semi-theoretical model

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extremely difficult. At high densities, the Modified Enskog theory [2], the excess viscosity function methods [4–6] and the friction theory (f-theory) [7] may be used for prediction of viscosity. Several estimation methods have been proposed for prediction of viscosity for organic compounds in literature such as, the Jossi–Stiel–Thodos correlation for non-polar pure substances [8], the Stiel–Thodos correlation for polar pure substances [9], method of Chung [10] and the modified method of Ely and Hanley [11]. Also, other methods such as the group contribution method [12] and artificial neural network [13], have been used for estimation of viscosity in terms of temperature.

In this work, the modified Enskog theory (MET) along with the modified linear isotherm regularity (MLIR) [14,15] are used to predict the viscosity of dense hydrocarbon fluids over wide ranges of temperature and pressure. Also, the principle of corresponding states is used to predict transport properties of dense fluids.

1.1. The modified Enskog theory

On the basis of the Enskog theory, viscosity of dense hard sphere fluid is given as [2]:

$$\eta = \eta_0 b_0 \rho \left[\frac{1}{Y} + 0.800 + 0.761Y \right] \quad (1)$$

where η is the viscosity of the hard-sphere fluid, η_0 the viscosity of a dilute hard sphere gas, b_0 the co-volume and is equal to $2/3\pi\sigma^3$, where σ is the hard-sphere diameter, and $Y = b_0 \rho g(\sigma)$, where ρ is the number density and $g(\sigma)$ is the two-body hard-sphere radial distribution function at contact. The quantity Y is related to the hard-sphere equation of state as

$$Y = \frac{p}{\rho kT} - 1 \quad (2)$$

Although the Enskog theory is an accurate theory for dense hard-sphere fluids, in which the pressure and the thermal pressure are the same, Enskog himself proposed and formulated its application to real dense fluids in an ad hoc manner. This transformation, which is known as the modified Enskog theory (MET), incorporates two modifications with respect to the original Enskog theory. First, Enskog suggested that instead of relating Y to the actual pressure of the system through Eq. (3), one should introduce the so called “thermal pressure”, $T(\partial p/\partial T)_\rho$, where $(\partial p/\partial T)_\rho$ is called the “thermal pressure coefficient”. The justification for this is that the contribution of the intermolecular interactions in pressure which is known as the “internal pressure”, $(\partial E/\partial V)_T$, must be included in the real fluids. The exact thermodynamic relation relates the sum of the pressure and the internal pressure to the thermal pressure as

$$T \left(\frac{\partial p}{\partial T} \right)_\rho = p + \left(\frac{\partial E}{\partial V} \right)_T \quad (3)$$

Therefore, Y may be written as

$$Y = \frac{1}{\rho RT} \left[T \left(\frac{\partial p}{\partial T} \right)_\rho \right] - 1 \quad (4)$$

Second, the co-volume b_0 is redefined in terms of the second and third virial coefficients B and C and their temperature derivatives:

$$b_0 = B + T \frac{dB}{dT} + C + T \frac{dC}{dT} \quad (5)$$

Therefore, having values of b_0 , η_0 , density and the thermal pressure coefficient, γ , of any real fluid along with the MET, the value of viscosity may be predicted at each temperature and pressure of interest. But, the latter step seriously hinders the application of the theory to real systems, because of a lack of knowledge of the virial coefficients for many fluids. On the other hand, the shortage of experimental data for the thermal pressure coefficients of liquids is another limitation in using the MET.

2. Viscosity calculation of dense fluids based on the MET

For prediction of viscosity of a dense fluid via Eq. (1), we need the values of b_0 , η_0 , density and the thermal pressure coefficient of that fluid. Precise information about the thermal pressure coefficient is scarce and obtained by cumbersome from the direct derivation of accurate equation of state which depends on fluid. The value of density may be obtained either by the exact equation of state or experimental data for a fluid. Also, the value of η_0 at any temperature may be found in literature for different compounds. Nevertheless, the lack of b_0 for many compounds is one of the main limitations in applying the MET to these systems. To solve this problem, we may make use of the hard sphere (HS) theory because of the fact that the behavior of a dense real fluid is primarily determined by the short range repulsive forces (like the HS fluid) and the relatively long-range attractive part of the potential provides a net force that gives a somewhat uniform attractive potential. To examine this point, we have calculated the thermal pressure of Xe using its accurate EOS [16], to plot the result against the pressure which is shown in Fig. 1. As shown in this figure, a linear correlation is found when $\rho > \rho_c$, unlike the case when $\rho < \rho_c$. In the other words, for a real dense fluid, the two pressures are not the same but they are different only by a constant for the entire density. So the values of b_0 and η_0 for dense fluids, may be approximately substituted from the HS theory. Therefore, we may rearrange Eq. (1) as:

$$\frac{\eta Y}{\eta_0 \rho} = b_0 (1 + 0.800Y + 0.761Y^2) \quad (6)$$

According to the kinetic theory of gases, the viscosity of a dilute hard sphere gas, η_0 , can be expressed as

$$\eta_0 = \frac{5}{16\sqrt{\pi}} \left(\frac{\sqrt{MRT}}{N_A \sigma^2} \right) \quad (7)$$

where M is the molecular weight, R the gas constant, T the temperature, N_A the Avogadro constant and σ is the hard-sphere diameter. By substituting this expression for η_0 and $2/3\pi\sigma^3$ for

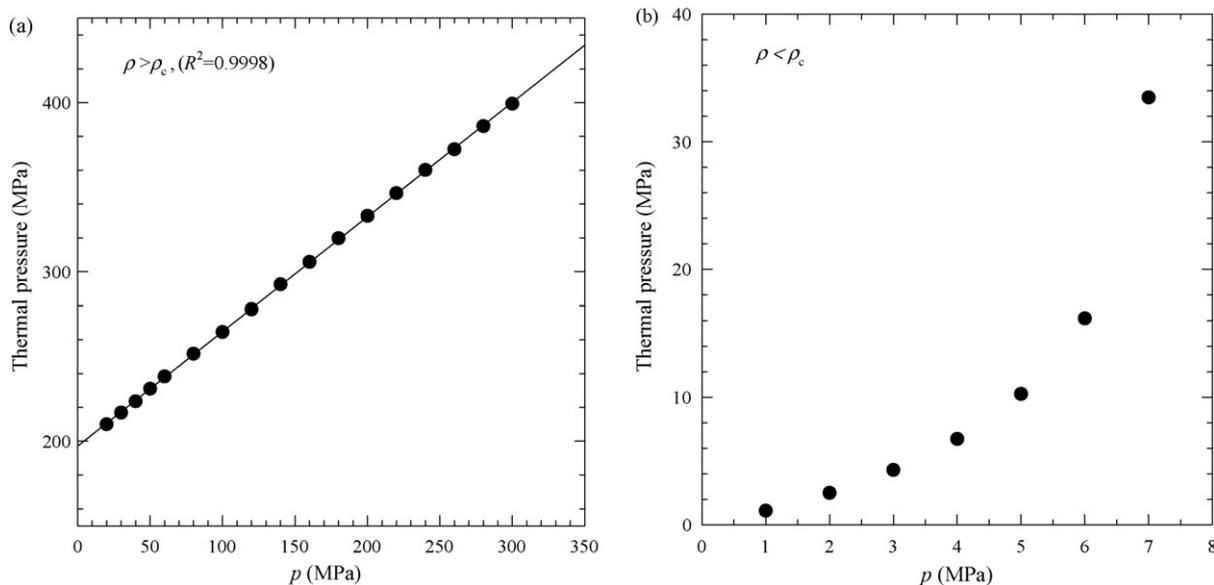


Fig. 1. Plot of the thermal pressure against the pressure of Xe for (a) $\rho > \rho_c$ and (b) $\rho < \rho_c$ at $T = 300$ K. Note the linear dependence of the two pressures in the former case, with the correlation coefficient $R^2 = 0.9998$.

b_0 in Eq. (6), this equation may be reduced to:

$$\begin{aligned} \frac{\eta Y}{\sqrt{T} \rho} &= \left(\frac{2}{3} \pi \sigma^3 \right) \left(\frac{5}{16 \sqrt{\pi}} \left(\frac{\sqrt{MR}}{N_A \sigma^2} \right) \right) \\ &\times (1 + 0.800Y + 0.761Y^2) \\ \Rightarrow \frac{\eta Y}{\sqrt{T} \rho} &= \left(\frac{5\sigma}{24} \left(\frac{\sqrt{\pi MR}}{N_A} \right) \right) (1 + 0.800Y + 0.761Y^2) \end{aligned} \quad (8)$$

or generally

$$\frac{\eta Y}{\sqrt{T} \rho} = aY^2 + bY + c \quad (9)$$

where a , b , and c coefficients are independent of temperature and expected to be so for the real dense fluids as well. However, they are expected to depend on temperature for real dilute fluids, due to appearance of σ on the right side of Eq. (8), even if Eq. (9) holds. To investigate our expectation, we select argon and xenon as test fluids because of the abundance of available experimental viscosity and pVT data and the existence of accurate equations of state for them. At first, by direct derivation from the accurate equations of state for Xe [16] and Ar [17], the values of thermal pressure coefficient may be obtained for these fluids. Then, using the calculated thermal pressure coefficient and experimental data for density [16,17] and viscosity [18,19] for different isotherms of these fluids, we have plotted $\eta Y / \sqrt{T} \rho$ versus Y , see Figs. 2 and 3. As shown in these figures, the quadratic fit holds quiet well for each isotherm with the correlation coefficient, $R^2 \geq 0.9993$, when $\rho > \rho_c$, where ρ_c is the critical density. In addition, these isotherms fall onto a single common quadratic curve for $\rho > \rho_c$ for whole temperature range that experimental data are reported ($200 \text{ K} < T < 600 \text{ K}$ for Xe and $110 \text{ K} < T < 500 \text{ K}$ for Ar). But as shown in Figs. 2 and 3b,

neither such common curve nor the quadratic fit are held when $\rho < \rho_c$. Due to significant deviation of real dilute fluids from the HS theory, such behaviors are expected. Since our purpose in this section is to predict viscosity of dense hydrocarbons, we have used Eq. (9) to investigate the prediction for n -alkanes from propane to n -octane and cyclohexane. To do so, at first, by direct derivation from the accurate equation of state for these compounds [20], the value of thermal pressure coefficient is obtained. Then, using the calculated thermal pressure coefficient and experimental data for density and viscosity of propane and n -butane [18], n -pentane, n -hexane, and n -octane [21], n -heptane [22] and cyclohexane [23] for different isotherms that experimental data are available, we have plotted $\eta Y / \sqrt{T} \rho$ versus Y . Again, we have found that plots of different isotherms for each of these fluids well fit in a quadratic function and all of them can be presented by a common curve at dense region, see Table 1. Therefore, the range of density and temperature over which this behavior is valid and a , b and c coefficients are independent of temperature, is $\rho > \rho_c$ and entire temperature range for which experimental data exist.

A common plot for $\eta Y / \sqrt{T} \rho$ in terms of Y resulted in, $\eta Y / \sqrt{T} \rho$ can be expressed by a quadratic function in terms of Y for each of these dense fluids with different values for the coefficients of the equation, see Eq. (9). The coefficients of this equation are given in Table 1 for Xe, Ar, n -alkanes from propane to n -octane and cyclohexane. Having these coefficients and the values of density and thermal pressure coefficient along with Eq. (9), the viscosity may be predicted in terms of pressure for each of these fluids. But as mentioned before, the experimental data for the thermal pressure coefficients are scarce and obtained from the direct derivation of accurate equation of state for different fluids. On the other hand, such accurate equation of state does not exist for many compounds. In this case, an appropriate EOS is desirable for calculation of both density and thermal pressure coefficient. Recently, the extension of linear isotherm regularity

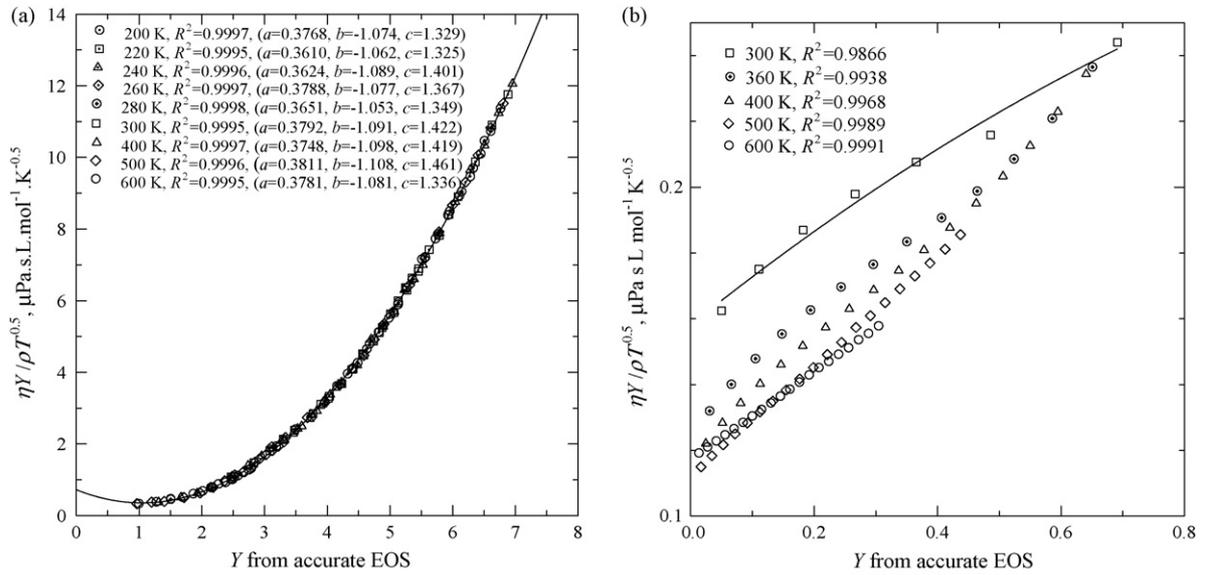


Fig. 2. Quadratic fit of $\eta Y / \rho \sqrt{T}$ as a function of Y for different isotherms of Xe for (a) $\rho > \rho_c$ and (b) $\rho < \rho_c$. The values of a , b , and c coefficients for each isotherm at $\rho > \rho_c$ are given in the parenthesis.

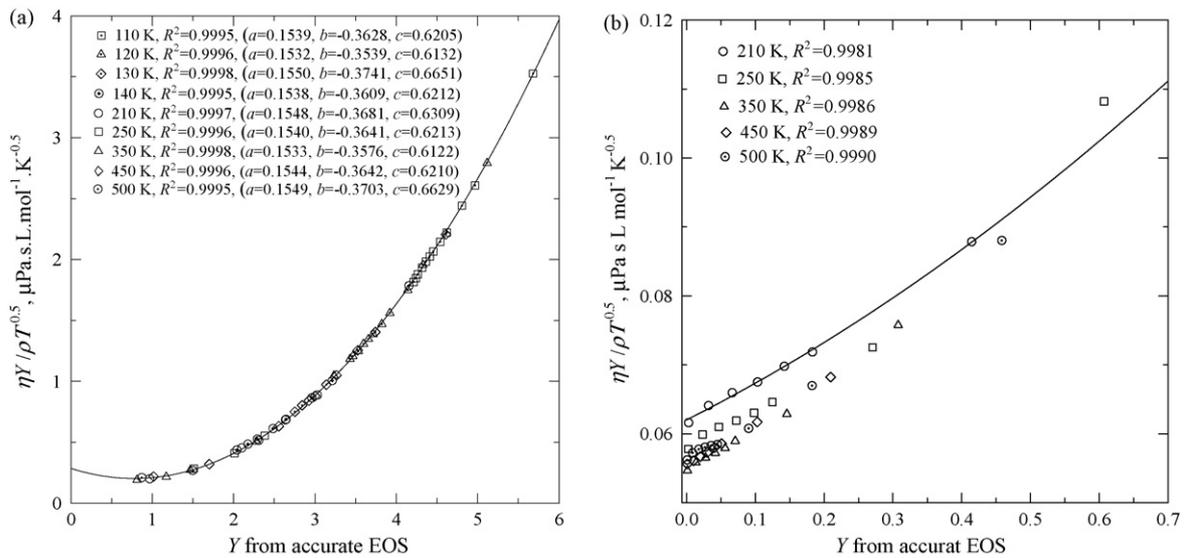


Fig. 3. Same as Fig. 1 for Ar.

Table 1

The values of a , b and c coefficients of Eq. (9) in $\mu\text{Pa.s.L.mol}^{-1}\text{K}^{-0.5}$ and the correlation coefficient, R^2 , for some given compounds obtained via fitting experimental data in Eq. (9) for given temperature and pressure ranges

Fluid	ΔT (K)	Δp (MPa)	a	b	c	R^2
C_3H_8	298.15–348.15	0.1–100	0.182	−0.838	2.318	0.9997
$n\text{-C}_4\text{H}_{10}$	298.15–348.15	0.1–69	0.269	−1.862	6.122	0.9998
$n\text{-C}_5\text{H}_{12}$	303.15–348.15	0.1–69	0.579	−7.668	33.899	0.9998
$n\text{-C}_6\text{H}_{14}$	303.15–348.15	0.1–92	0.912	−14.755	73.984	0.9998
$n\text{-C}_7\text{H}_{16}$	303–348	0.1–100	1.377	−25.638	154.005	0.9997
$n\text{-C}_8\text{H}_{18}$	303.15–348.15	0.1–96	1.956	−45.819	309.464	0.9997
C_6H_{12}	298.15–348.15	0.1–85.5	4.893	−100.993	558.620	0.9997
Xe	200–600	20–300	0.380	−1.0986	1.449	0.9996
Ar	110–500	0.1–400	0.1543	−0.3639	0.6211	0.9996

to long chain organic compounds is reported via the group contribution method [14,15]. We may use this EOS (known as the modified linear isotherm regularity, MLIR) for prediction of density and thermal pressure coefficient of hydrocarbons because of its high performance. The MLIR used in this work is going to be introduced in brief.

2.1. The modified linear isotherm regularity equation of state

Using the LJ (12, 6) potential for the average effective pair potential (AEPP) along with the pairwise additive approximation for the molecular interactions in dense fluids and considering only the nearest neighbor interactions, the linear isothermal regularity (LIR) was derived from the exact thermodynamic relations as

$$(Z - 1)v^2 = A + B\rho^2 \quad (10)$$

where $Z = p/\rho RT$ is the compressibility factor, and $\rho = 1/v$ is the number density and A and B are the temperature dependent parameters [24]. The LIR was experimentally found to be hold for all types of fluids for densities greater than the Boyle density ($\rho_B \approx 1.8\rho_c$, where ρ_c is the critical density) and temperature less than twice the Boyle temperature. Since the mathematical form of the AEPP function is assumed to be the LJ (12,6), such potential function is appropriate for the spherical-symmetrical molecules, then non-spherical molecules, such as the chain organic compounds, show significant deviation from the linearity of the LIR. However, based on the group contribution method concept, an organic compound may be considered as a hypothetical mixture of their constituent groups, in which the interaction potential among any two groups is assumed to be the AEPP. Then, on the basis of the van der Waals one-fluid approximation, the LIR equation of state was used for such a hypothetical mixture, but the new equation of state parameters in addition of temperature, depend on groups composition of the mixture. Therefore, the LIR for ordinary mixtures [25] was extended to organic chains as [15]:

$$\begin{aligned} \left(\frac{p}{n\rho RT} - 1 \right) &= A_m + B_m n^2 \rho^2 \\ \Rightarrow \left(\frac{Z}{n} - 1 \right) &= A_m + B_m n^2 \rho^2 \end{aligned} \quad (11)$$

which we shall refer to it as the modified linear isotherm regularity (MLIR) from now on. In this equation, A_m and B_m are the MLIR parameters where their temperature dependencies are just the same as those for the LIR parameters and n is the number of constituent groups of organic compound. In our previous works the MLIR were successfully applied for long chain organic compounds such as n -alkanes and their binary mixtures [14], primary, secondary and tertiary alcohols, ketones and 1-carboxylic acids [15], according to which $(Z/n - 1)v^2$ is linear against ρ^2 for each isotherm of these dense fluids. The MLIR parameters (A_m , B_m) for these fluids were predicted by using the group contribution method. To do so, we considered each of

these fluids as a hypothetical mixture of its constituent groups, namely methyle, terminal methylene (methylene groups each attached to one methyle group), middle methylene (methylene groups at the middle of chain which each of them attached to two methyle groups), and an appropriate functional group such as $-\text{CH}_2\text{OH}$, >CHOH , $\begin{array}{c} -\text{C}\text{OH} \\ | \end{array}$, >C=O , and $-\text{COOH}$ groups. Then basic compounds, namely propane and n -butane, were used to obtain the contribution of methyl and terminal methylene groups, cyclohexane was used to obtain the contribution of the middle methylene groups and also other appropriate compounds were used to obtain the contribution of the functional groups in the MLIR parameters. Having the contribution of constituent groups in the EOS parameters along with dependencies of the LIR parameters to system composition, the MLIR parameters for each compound were calculated. The calculated EOS parameters along with the MLIR are then used to calculate the density of different organic compounds at different pressures and temperatures with the average percentage error less than 1.2. Also, we have calculated the thermal pressure coefficient ($\gamma = (\partial p/\partial T)_\rho$) at different temperatures and pressures for some hydrocarbons from the following expression obtained from the MLIR with average percentage error less than 1.1%:

$$\begin{aligned} \left(\frac{\partial p}{\partial T} \right)_\rho &= n\rho R + n^3 \rho^3 R(A_m + A'_m T) + n^5 \rho^5 R(B_m \\ &+ B'_m T) \end{aligned} \quad (12)$$

The main advantage of the MLIR for organic dense fluids is that we may predict their density and thermal pressure coefficient accurately, just by using the experimental data of the basic compounds. Hence, we have used this EOS to calculate density and thermal pressure coefficient of dense hydrocarbons.

2.2. Viscosity calculation using the quadratic expression along with the MLIR-EOS

The main purpose in this section is to calculate the viscosity of n -alkanes from propane to n -octane and cyclohexane in terms of pressure and temperature using Eq. (9) and the MLIR. For this purpose, the contribution of three constituent groups of these fluids (methyle, terminal methylene and middle methylene) in the MLIR parameters, were calculated using three basic compounds, namely propane, n -butane and cyclohexane at 313.15 and 333.15 K (for details see Refs. [14,15]). Having the contributions of three constituent groups of the EOS parameters along with dependencies of the LIR parameters to system composition, the MLIR parameters for each n -alkane and cyclohexane were calculated at two temperatures. Then, using the calculated MLIR parameters along with Eqs. (11) and (12), the density and thermal pressure coefficient have been calculated for each of them in terms of pressure at both temperatures. The calculated values of density and thermal pressure coefficient, and also the coefficients of Eq. (9) for each of these hydrocarbons given in Table 1 may be used to calculate viscosity coefficient at any pressure and temperature. The calculated results are given in

Table 2

Average absolute percent deviation of the calculated viscosity for *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and cyclohexane at 313.15 and 333.15 K using the calculated values of density and thermal pressure coefficient obtained from the MLIR and the values of *a*, *b* and *c* coefficients of Eq. (9) from Table 1

Fluid	<i>T</i> (K)	$\Delta\rho$ (MPa)	$(\Delta\eta /\eta)_{av} \times 100$
<i>n</i> -C ₄ H ₁₀	313.15		0.75 (0.99)
	333.15	0.1–69	0.81 (1.1)
<i>n</i> -C ₅ H ₁₂	313.15		0.89 (1.2)
	333.15	0.1–69	0.96 (1.3)
<i>n</i> -C ₆ H ₁₄	313.15		0.99 (1.4)
	333.15	0.1–92	1.1 (1.5)
<i>n</i> -C ₇ H ₁₆	313.15		1.0 (1.4)
	333.15	0.1–100	1.2 (1.7)
<i>n</i> -C ₈ H ₁₈	313.15		1.5 (1.9)
	333.15	0.1–96	1.6 (2.0)
C ₆ H ₁₂	313.15		0.91 (1.2)
	333.15	0.1–85.5	0.98 (1.3)

Maximum deviations are given in parentheses.

Table 2. The average percentage error and its maximum value for viscosity were found to be lower than 1.6 and 2.0, respectively.

3. Extension to other transport properties

3.1. Calculation of thermal conductivity

Based on MET, the thermal conductivity of a dense fluid is given as [2]:

$$\lambda = \lambda_0 b_0 \rho \left[\frac{1}{Y} + 1.2 + 0.755Y \right] \quad (13)$$

where λ is the thermal conductivity of the dense fluid, λ_0 is its zero density value, b_0 is the co-volume, ρ is the number density and Y for real dense fluid may be given by Eq. (4). Again, the values of λ_0 and b_0 may be substituted from dilute gas expressions of the hard sphere fluids. Based on the kinetic theory of gases, the zero-density thermal conductivity of hard sphere gas, λ_0 , can be given as [2]:

$$\lambda_0 = \frac{5}{16} \left(C_{V,m} + \frac{9}{4}R \right) \left(\frac{RT}{\pi M} \right)^{1/2} \frac{1}{N_A \sigma^2} \quad (14)$$

where $C_{V,m}$ is the molar heat capacity at constant volume. By substituting this expression for λ_0 and $2/3\pi\sigma^3$ for b_0 in Eq. (13), this equation may be reduced to

$$\frac{\lambda Y}{\rho \sqrt{T} (C_{V,m} + (9/4)R)} = iY^2 + jY + k \quad (15)$$

where *i*, *j* and *k* coefficients are independent of temperature and expected to be so for real dense fluids as well. The same as previous section, we may expect that the plot of $\lambda Y/\sqrt{T}\rho(C_{V,m} + (9/4)R)$ in terms of Y be quadratic for each isotherm of a dense fluid and the isotherms fall onto a common curve. To investigate this expectation, we may use the experimental data of density and thermal conductivity of Xe [16,18] because of the abundance of available experimental thermal conductivity and pVT data and its reported accurate equation of state [16]. For the monoatomic fluids, $C_{V,m}$ is almost independent of temperature and hence we

expect that plots of $\lambda Y/\sqrt{T}\rho$ in terms of Y be quadratic for each isotherm of Xe. As shown in Fig. 4a and b, for $\rho > \rho_c$, the data for each isotherm fit well in a quadratic function and in addition to that all isotherms fall onto a single curve for all isotherms for which experimental data exist. However, neither the quadratic fit nor the falling onto a common curve were observed when $\rho < \rho_c$. Therefore, if $\lambda Y/\sqrt{T}\rho(C_{V,m} + 9/4R)$ is plotted in terms of Y for any isotherm of a dense fluid and fitted in a quadratic equation, the obtained coefficients of the equation may be used to calculate the thermal conductivity of that fluid at any other temperature. Therefore, again we may use the MLIR to calculate density and thermal pressure coefficient, along with the coefficients of Eq. (15), to calculate λ for dense organic compounds. Unfortunately, there is no enough experimental data in literature to do such calculation.

3.2. Calculation of self-diffusion

The self-diffusion is given as [2]:

$$D = D_0 b_0 \rho \left(\frac{1}{Y} \right) \quad (16)$$

where D is the self-diffusion of the hard-sphere fluid, D_0 the self-diffusion of a dilute hard sphere gas, b_0 the co-volume and ρ is the number density. Again, the quantity of Y for real dense fluid may be given by Eq. (4) and the self-diffusion of a dilute hard sphere gas, D_0 , is obtained from the kinetic theory of gases as [2]:

$$D_0 = \frac{3}{8} \left(\sqrt{\frac{RT}{\pi M}} \right) \frac{1}{\rho \sigma^2} \quad (17)$$

By substituting this expression for D_0 and $2/3\pi\sigma^3$ for b_0 in Eq. (16), this equation may be reduced and rearranged to:

$$D = \frac{3}{8} \left(\sqrt{\frac{RT}{\pi M}} \right) \frac{1}{\rho \sigma^2} \left(\frac{2}{3}\pi\sigma^3 \right) \rho \left(\frac{1}{Y} \right) \\ \Rightarrow \frac{DY}{\sqrt{T}} = \frac{\sigma}{4} \sqrt{\frac{R\pi}{M}} \quad (18)$$

or generally

$$\frac{DY}{\sqrt{T}} = \text{cte} \quad (19)$$

For the self-diffusion we expect that plots of DY/\sqrt{T} versus Y for each isotherm of dense fluid to be a constant. To test such an expectation, we have used the self-diffusion data of methane [26] and *n*-hexane [27], only available data we could find in literature. By the direct derivation of the accurate equation of state of methane and *n*-hexane [20], the value of thermal pressure coefficient is calculated. Then, using the calculated thermal pressure coefficient and experimental data for self-diffusion of methane and *n*-hexane for each isotherm for which the experimental data exists, we have plotted DY/\sqrt{T} versus Y , see Fig. 5a and b. As shown in Fig. 5a, the data of different isotherms for each fluid are well fitted in a single line when $\rho > \rho_c$ and $T < T_c$, instead of

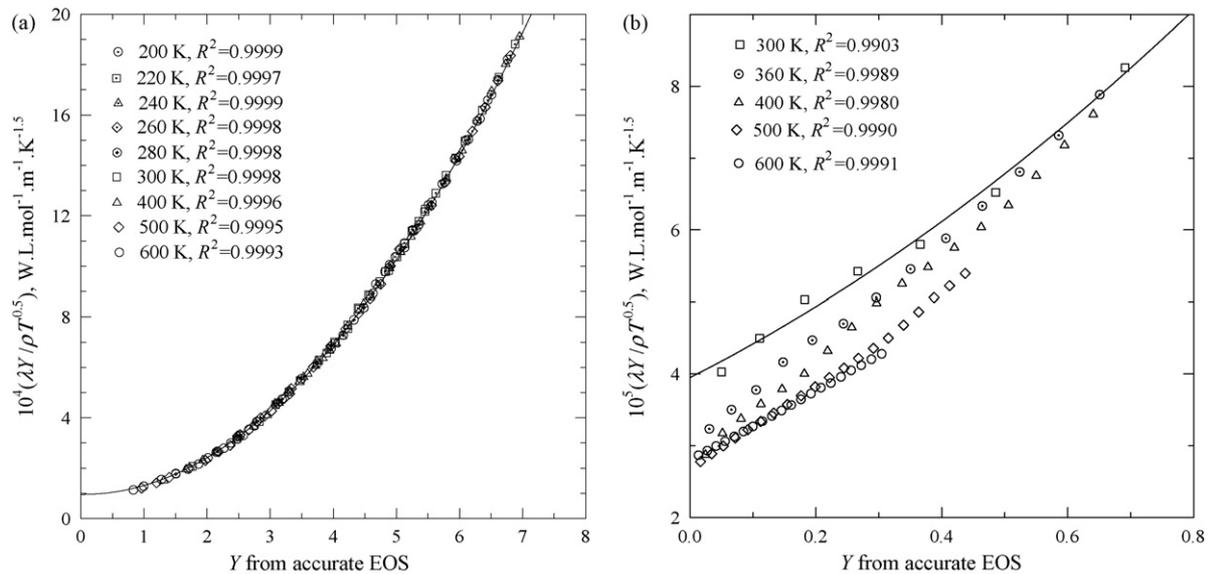


Fig. 4. Quadratic fit of $(\lambda Y/\rho\sqrt{T})$ vs. Y for different isotherms of Xe for (a) $\rho > \rho_c$ and (b) at $\rho < \rho_c$.

being a constant. However for the supercritical isotherms (even with $\rho > \rho_c$) shown in Fig. 5b, neither the linearity nor the falling of isotherms onto a single curve are observed. Therefore, we may expect that having the intercept and slope of the line for a fluid are sufficient to be used along with the MLIR, to calculate the self diffusion coefficient of that fluid when $\rho > \rho_c$ and $T < T_c$.

4. Viscosity calculation of dense fluids using the principle of corresponding states

As mentioned in the previous section, the values of a , b and c coefficients in Eq. (9) depend on fluid. However, they are independent of temperature for the dense fluids ($\rho > \rho_c$). Therefore, for the dense fluids, at least experimental data for one isotherm and accurate EOS for calculation of the thermal pressure coef-

ficient are need. However, for the latter need, the MLIR and group contribution method may be used. If there is no experimental data, even for one isotherm of a fluid, we may make use of the principle of corresponding states for the prediction of viscosity of the dense fluid over a wide temperature and pressure ranges. To do so, we reduce η , T , and ρ by η_0 , T_c and ρ_c , respectively. Therefore, Eq. (9) may be written in the reduced form as,

$$\frac{\eta_r Y}{\sqrt{T_r} \rho_r} = a' Y^2 + b' Y + c' \quad (20)$$

where a' , b' and c' coefficients are expected to be independent of fluid, but depend on T_r . For checking such expectation, the experimental values of density and viscosity along with the thermal pressure coefficient calculated from the accurate EOS for

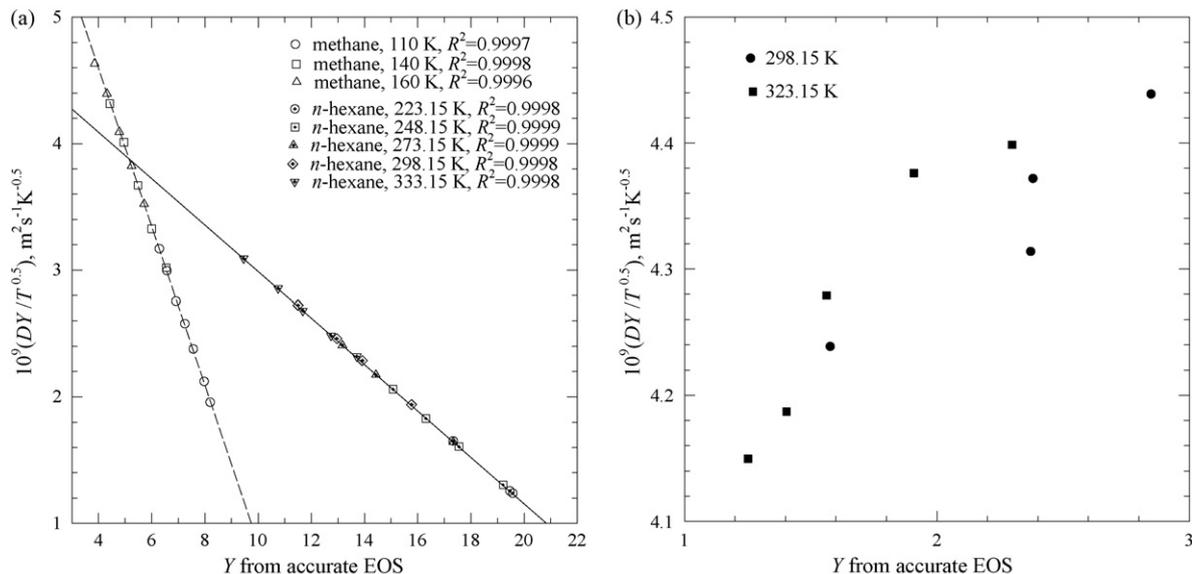


Fig. 5. Plot of DY/\sqrt{T} vs. Y for given isotherms with $\rho > \rho_c$ of (a) methane (dashed line) and n -hexane (solid line) when $T < T_c$ and for (b) methane with $T < T_c$.

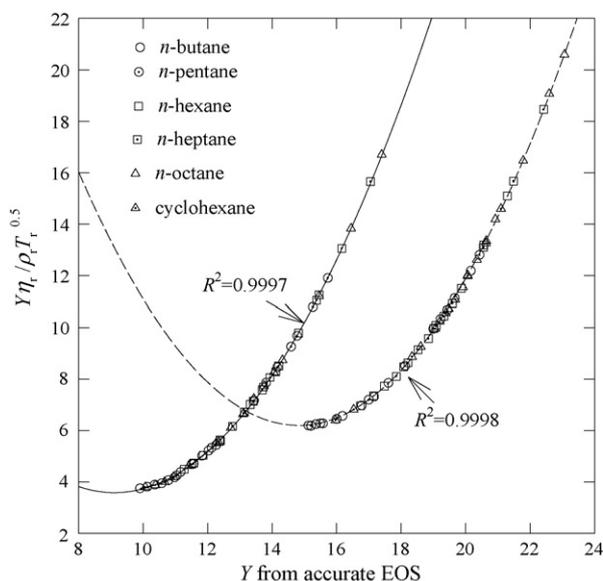


Fig. 6. Quadratic fit of $\eta_r Y / \rho_r T_r^{0.5}$ vs. Y for n -butane, n -pentane, n -hexane, n -heptane, n -octane and cyclohexane for $T_r = 0.45$ (dashed line) and $T_r = 0.6$ (solid line) isotherms.

n -alkanes (C_4 – C_8), are used to plot the dimensionless quantity $\eta_r Y / \rho_r \sqrt{T_r}$ versus Y at two reduced temperatures ($T_r = 0.45, 0.6$), see Fig. 6. As shown, all the points for a given T_r fall on a single quadratic curve with the correlation coefficient $R^2 > 0.9996$. Therefore, one may use the experimental data for one isotherm of an arbitrary fluid to find the a' , b' , and c' coefficients of Eq. (20). Then, these coefficients may be used for other fluids at the same reduced temperature as well. Here, we have selected n -butane as a reference compound, because of the abundance of experimental data for it over a wide range of temperature and pressure. The experimental values of density and viscosity [18] along with the thermal pressure coefficient calculated from its accurate EOS [20] of n -butane are used to obtain the values of a' , b' , and c' coefficients at $T_r = 0.55$ ($a' = 0.197$, $b' = -4.401$ and $c' = 30.472$). We have used these values along with the calculated values of density and thermal pressure coefficient from the MLIR at this reduced temperature to obtain viscosity at $T_r = 0.55$ for some other hydrocarbons with the average percentage error less than 1.7, see Table 3.

This approach has not been applied for the thermal conductivity and self diffusion because of the lack of experimental data

Table 3

Average absolute percent deviation of the calculated viscosity for n -pentane, n -hexane, n -heptane, n -octane and cyclohexane at $T_r = 0.55$ using the calculated values of density and thermal pressure coefficient obtained from the MLIR and Eq. (20) for which its coefficients are obtained from experimental data of n -butane

Fluid	T (K)	Δp (MPa)	$(\Delta\eta /\eta)_{av} \times 100$
n - C_5H_{12}	258.34	0.1–69	0.98 (1.2)
n - C_6H_{14}	279.30	0.1–92	1.1 (1.4)
n - C_7H_{16}	297.07	0.1–100	1.4 (1.7)
n - C_8H_{18}	313.13	0.1–96	1.7 (2.1)
C_6H_{12}	304.48	0.1–85.5	1.2 (1.6)

Maximum deviations are given in parentheses.

for these transport properties. However, we expect that the principle of corresponding states may be applied for these properties as well, at least for non-polar and weakly polar fluids.

5. Conclusions

In this work, the MET expressions and their zero density HS expressions are used to obtain a simple linear expression (for self diffusion) and quadratic expressions, Eq. (9) for viscosity and Eq. (16) for thermal conductivity, in terms of $Y = [T(\partial p/\partial T)_\rho]/\rho RT - 1$ at high densities ($\rho > \rho_c$) at which real fluids approximately behave more and less like a HS fluid. The obtained expressions are generally valid for the real dense fluids but the ratios of coefficients are different from those of the HS fluid. However, real fluids, as expected, behave quite differently with HS fluid at low densities ($\rho < \rho_c$), in such a way that the linear and quadratic expressions of the HS fluid are not valid any more. We have approved such behavior by using experimental data. To evaluate such approval, experimental data for density and viscosity and calculated thermal pressure coefficient from an accurate EOS, were used to plot $\eta Y / \sqrt{T} \rho$ against Y for Xe and Ar, see Figs. 2 and 3. The quadratic fit holds quite well with the correlation coefficient $R^2 \geq 0.9995$, for these compounds at high densities ($\rho > \rho_c$), see Figs. 2 and 3a. Also, we have noticed that the plots for different isotherms of a dense fluid fall onto a common curve, see Figs. 2 and 3a, but such behavior weren't observed at low densities ($\rho < \rho_c$) for which the effect of the attractive forces are more important and hence deviation from the HS fluid is significant, see Figs. 2 and 3b. The temperature range of the quadratic fit and falling of the isotherms onto a single curve were observed over a wide range of temperature and pressure (200 < T < 600 K and pressure up to 300 MPa for Xe and 110 K < T < 500 K and pressure up to 400 MPa for Ar) that is the entire temperature range for which the experimental data are reported. Also, this approach was applied to the dense hydrocarbons and a , b , and c coefficients of Eq. (9) were calculated and tabulated, see Table 1. Calculation of viscosity by using Eq. (9) requires the values of density, thermal pressure coefficient, and a , b , and c coefficients. The values of the coefficients for each of these fluids may be found in Table 1. Also, the values of density and thermal pressure coefficient may be calculated from the MLIR and its appropriate derivative using the group contribution method. Using these coefficients along with the calculated values of density and thermal pressure coefficient from the MLIR, viscosity of the hydrocarbons at two temperatures, 313.15 and 333.15 K, were calculated with average percentage error lower than 1.6, see Table 2. Also, the calculated viscosity of some hydrocarbons are compared with those of some correlations [8,10,11] for a given temperature and pressure range, in Table 4.

This approach has been extended and evaluated for other transport properties such as the thermal conductivity, λ , and self-diffusion, D . For the thermal conductivity, the accuracy of the quadratic expression was investigated using the calculated thermal pressure coefficient from the accurate equation of state and experimental data for density and thermal conductivity of Xe. We have again found that $\lambda Y / \sqrt{T} \rho$ in terms of

Table 4
Comparison of average absolute percent deviation of the calculated viscosity obtained from this work with those obtained from several estimation methods [8,10–11] at given temperature and pressure ranges

Fluid	ΔT (K)	Δp (MPa)	$100(\Delta\eta /\eta)_{av}$			
			This work	Thodos [8]	Chung [10]	Ely and Hanely [11]
<i>n</i> -C ₄ H ₁₀	280–350	0.1–65	1.03 (1.27)	9.5 (28.4)	6.5 (28.6)	5.9 (27.1)
<i>n</i> -C ₅ H ₁₂	313.15–348.15	0.1–69	1.18 (1.32)	12.8 (28.1)	6.6 (16.7)	3.9 (19.9)
<i>n</i> -C ₆ H ₁₄	298.15–348.15	0.1–92	1.31 (1.58)	14.7 (30.8)	7.8 (18.3)	5.8 (80.4)
<i>n</i> -C ₇ H ₁₆	303–348	0.1–100	1.50 (1.81)	12.8 (28.8)	4.7 (20.5)	3.3 (31.6)
<i>n</i> -C ₈ H ₁₈	298.03–348.14	0.1–96	1.84 (2.23)	13.4 (23.8)	3.5 (14.7)	4.4 (14.6)
C ₆ H ₁₂	298.15–348.15	0.1–85.5	1.24 (1.45)	49.9 (54.2)	47.4 (65.9)	46.1 (66.4)

Maximum deviations are given in parentheses.

Y for different isotherms of Xe fits in a quadratic expression with $R^2 > 0.999$ when $\rho > \rho_c$. The same as that for viscosity, the isotherms fall onto a single quadratic curve at high densities ($\rho > \rho_c$), see Fig. 4a, but such behavior are not observed at low densities ($\rho < \rho_c$), see Fig. 4b. Again, at low densities that attractive forces become more important than repulsive ones, deviation from the HS fluid is expected to be significant. For the self diffusion, the quantity DY/\sqrt{T} for the HS fluid does not vary with Y . To investigate such a case for real fluids, the calculated values of the thermal pressure coefficient from the accurate equation of state and experimental data for density and self-diffusion of methane and *n*-hexane have been used to plot DY/\sqrt{T} versus Y . As shown in Fig. 5a, we have found that the data for each isotherm of subcritical fluid fit in a linear expression and at high densities ($\rho > \rho_c$) they fall onto a single line. However, neither the linearity nor the falling was observed for the supercritical fluids, even at high densities ($\rho > \rho_c$), see Fig. 5b. It seems that diffusion of molecules in a supercritical dense fluid is quiet different with that of the subcritical dense fluid, compare Fig. 5a with b.

Even though a real dense fluid behaves according to the mathematical expression obtained for the properties of the HS fluid, but their behavior is not exactly the same, for this reason the ratios of the coefficients for the expressions obtained for real fluids are different with those of the HS fluid. Each molecule in the dense fluid experiences mainly a repulsion which is somewhat soft, compare to infinite value for the HS molecule when two molecules penetrate each other. Therefore, one may expect that real dense fluids behave similar to HS fluid, but their behaviors are not exactly the same.

For calculation of viscosity and thermal conductivity of a dense fluid via the quadratic equations, Eq. (9) for the viscosity and Eq. (15) for the thermal conductivity, we need the experimental data at least for one isotherm of that fluid and an accurate EOS for calculation of its thermal pressure to obtain the coefficients of the quadratic equations, because the values of the coefficients in the quadratic equations depend on type of fluid. Therefore, if there is no experimental data even for one isotherm of that fluid, this approach cannot be used. In this case, we may resort to the principle of corresponding states. For this purpose, we have reduced η , T , and ρ in Eq. (9) by η_0 , T_c and ρ_c , respectively. Thus, a' , b' , and c' of Eq. (20) are being independent of fluid type at a given reduced temperature. Using the experimental values of density, viscosity and thermal pressure coefficient

of *n*-alkanes (C₄–C₈), the universality of Eq. (20) is verified for two reduced temperatures ($T_r = 0.45, 0.60$), for which the experimental data are available, see Fig. 6. As shown in this figure, at any reduced temperature, dimensionless quantity $\eta_r Y / \rho_r \sqrt{T_r}$ versus Y fits in a single quadratic curve ($R^2 > 0.9996$) for all given hydrocarbons. Therefore, by fitting the data of a real fluid at a given reduced temperature in the quadratic function in terms of Y , the coefficients (a' , b' , and c') may be used for other fluids at the same reduced temperature. We have selected *n*-butane as a reference fluid because of abundance of pVT and viscosity data. Using its experimental values of density, viscosity and thermal pressure coefficient, the values of a' , b' , and c' coefficients at $T_r = 0.55$ are obtained. Having the values of these coefficients and calculating the values of density and thermal pressure coefficient from the MLIR at this reduced temperature for other fluids, we have calculated viscosity of some hydrocarbons with the average percent error less than 1.7%, see Table 3.

We may also use the principle of corresponding states to calculate thermal conductivity and self-diffusion by a similar procedure mentioned for viscosity. However, because of limited data for such properties of organic compounds, we have not calculated them. Also, the procedure may be applied for other compounds, at least for non-polar and slightly polar compounds.

List of symbols

a, b and c	coefficients of Eq. (9)
a', b' and c'	coefficients of Eq. (20)
A, B	LIR parameters
A_m, B_m	MLIR parameters
b_0	co-volume
B_2, C	second and third virial coefficients
D	self-diffusion
D_0	self-diffusion of a dilute hard sphere gas
$g(\sigma)$	two-body hard-sphere radial distribution function at contact
i, j and k	coefficients of Eq. (15)
M	molecular weight
n	total number of constituent groups of organic compound
N_A	Avogadro constant
p	pressure
R	gas constant
T	temperature
$T(\partial p/\partial T)_\rho$	thermal pressure

T_c critical temperature
 T_r reduced temperature
 $Z = p/\rho RT$ compressibility factor

Greek symbols

$\gamma = (\partial p/\partial T)_\rho$ thermal pressure coefficient
 $(\partial E/\partial V)_T$ internal pressure
 η viscosity
 η_r reduced viscosity
 η_0 viscosity of a dilute hard sphere gas
 λ thermal conductivity
 λ_0 thermal conductivity of a dilute hard sphere gas
 ρ number density
 ρ_c critical density
 ρ_r reduced density
 σ hard-sphere diameter

Acknowledgment

Financial support for this work by the research consul of the Isfahan University of Technology is gratefully acknowledged.

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