Extended Hard-Sphere Model for Predicting the Viscosity of long-chain *n*-alkanes

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Abstract

An extended hard-sphere model is presented that can accurately and reliably predict the viscosity of long chain *n*-alkanes. The method is based on the hard-sphere model of Dymond and Assael, that makes use of an universal function relating reduced viscosity to reduced volume. The existing expression for the molar core volume is extrapolated to long chain *n*-alkanes, while the roughness factor is determined from experimental data. A new correlation for roughness factor is developed that allows the extended model to reproduce the available experimental viscosity data on long chain *n*-alkanes up to tetracontane (*n*-C₄₀H₈₂) within ± 5 %, at pressure up to 30 MPa. In the dilute gas limit a physically realistic model, based on Lennard-Jones effective potential, is proposed and used to evaluate the zero-density viscosity of *n*-alkanes to within ± 2.4 %, that is better than currently available.

Keywords

Alkanes; Correlation; Hard-Sphere Theory; High Pressure; Liquid; Vapour; Viscosity.

1. Introduction

Normal, paraffinic alkanes (*n*-alkanes) of generic chemical formula C_nH_{2n+2} are an important constituent of oil and are ubiquitous in petroleum and chemical processes. In numerous industrial applications that involve the flow of fluids, knowledge of the viscosity of *n*-alkanes and their mixtures is an essential pre-requisite for good design and optimal operations [1-2]. For a number of *n*-alkanes (methane to *n*-butane, *n*-hexane to *n*-octane, *n*-decane, *n*-dodecane) [3-10] there exist accurate and reliable correlations of viscosity that cover a wide range of temperatures and pressures, with well-defined estimates of uncertainty. Such correlations are based on the best available experimental data, selected on the basis of a critical analysis of the measurement methods and complemented with guidance, to the functional form of the correlation, available from theory. For *n*-alkane molecules that consist of longer carbon chains the experimental viscosity data are scarce and it is not possible to produce reliable correlations. Thus, one needs to develop generic, predictive models that can supplement current gaps in the viscosity data for pure *n*-alkanes. Not only are such values useful in their own right, but they also serve as the starting point for the prediction of viscosity of mixtures [1]. In case of mixtures containing *n*-alkanes the addition of long-chain *n*-alkane species will increase viscosity significantly, thus further necessitating a reliable knowledge of viscosity.

For engineering purposes the reliability of a predictive model is best achieved if the model has some basis in the underlying physical theory, so that it can be safely used for different fluids over a wide range of temperature and pressure. Although kinetic theory [11] provides such an underlying theory, that in principle allows for a link to be established between viscosity and molecular properties, it is only possible to evaluate viscosity, by means of kinetic theory, at a low-density in the gaseous phase. In the case of *n*-alkanes, only for methane has the kinetic theory been used in conjunction with an ab-initio intermolecular potential to predict the viscosity in the dilute gas limit, with accuracy that is commensurate

with the best experimental data [12]. For dense fluids the only tractable solutions developed to date are based on the assumption that the molecules interact as hard spheres and that their collisions are uncorrelated. The resulting Enskog equation [13] for the viscosity of a dense hard-sphere fluid has formed the basis for several semi-theoretical approaches, two of which in particular have found practical application: the Dymond and Assael (DA) approach [14-19] and the Vesovic-Wakeham (VW) model [20-23]. In this work we focus on the DA approach with the objective of extending its versatility, so that we can predict the viscosity of pure, long-chain *n*-alkanes. We see this as a precursor to further refining the VW approach, which requires the viscosity of pure species, in order to predict the viscosity of mixtures of relevance to the petro-chemical industry.

The DA model [14-19] is based on the observation that the viscosity of real fluids can be mapped onto a universal function by an appropriate choice of two parameters, the core volume and the roughness factor. Although for hard-spheres the core volume, which corresponds to the close-packed volume is athermal, for real fluids a temperature dependence was introduced [14] to account for the fact that the molecules interact through intermolecular potential that contains both repulsive and attractive parts. For *n*-alkanes both the core volume and the roughness factor exhibit a smooth behaviour and were fitted to a function of temperature and carbon number, respectively. The resulting model [14] can reproduce the viscosity of the first sixteen pure *n*-alkanes within $\pm 5\%$. Ciotta et al. [24] extended the original DA model so that it behaves correctly in the limit of low densities and offers improved accuracy at high densities. By making use of a large database of experimental viscosities, that contains many measurements not available at the time of the development of the original DA model, Ciotta et al. [24] updated the universal reference function, thus extending the range of the model up to reduced densities, defined with respect to the core volume, of approximately 0.9. In this work we have made use of this extended hard-sphere model to propose a modification that allows the use of the DA model for predictions of the viscosity of long chain *n*-alkanes longer than octadecane, which was the

longest n -alkane considered by Ciotta et al. [24]. Although we have focused on viscosity models that have their origins in kinetic theory, there are many other approaches that make use of corresponding-states principle, exploit the links with thermodynamics or are based on realistic detailed and coarse-grain molecular simulations that can and have been used to predict the viscosity of alkanes. The interested reader is referred to Ref [1] that covers the recent advances in the field for more details.

In section 2 we briefly summarize the extended hard-sphere model and introduce the modifications made in the treatment of zero-density viscosity and the roughness factor. In section 3 first we present the results for the zero-density viscosity of long chain n -alkanes and follow it by describing the development and testing of the proposed model for the prediction of the viscosity of pure, long-chain n -alkanes as a function of density.

2. Methodology

2.1 The Extended Hard-Sphere Model

As mentioned in the introduction, the recently proposed extended hard-sphere model [24] is the latest modification of the original hard-sphere model of Dymond, Assael and their collaborators [14-18]. As it forms the basis of the developments presented in this work we will briefly summarize its main features. The extended hard-sphere model makes use of a reduced excess viscosity, $\Delta\eta^*$, defined as [24],

$$\Delta\eta^* \equiv \frac{16}{5}(2N_A)^{1/3} \left(\frac{\pi}{MRT} \right)^{1/2} V_m^{2/3} \left(\frac{\eta - \eta_0}{R_\eta} \right) = 0.661812 \left(\frac{1}{MT} \right)^{1/2} V_m^{2/3} \left(\frac{\eta - \eta_0}{R_\eta} \right), \quad (1)$$

where V_m is the molar volume, M is the molar mass, N_A is Avagadro's constant, R is the gas constant, R_η is the roughness factor and η and η_0 , are viscosity and viscosity in the zero-density limit, respectively. The second part of the equation provides a more practical expression where the molar volume and the viscosity are in the units of $\text{cm}^3 \cdot \text{mol}^{-1}$ and $\mu\text{Pa} \cdot \text{s}$, respectively. The reduced excess viscosity has the correct behaviour as the density tends to zero which ensures that the model behaves reasonably when extrapolated to densities lower than liquid-like densities, unlike the original hard-sphere model [14-18] which was only valid for compressed gas and liquid state. The model makes use of the assumption that the reduced viscosity is an universal function of the reduced molar volume, $V^* = V_m/V_0$. For a hard-sphere fluid, the parameter V_0 is simply the molar volume of the close-packed arrangement of hard spheres. For real fluids, where the molecules interact through sometimes complex interaction potentials, V_0 is treated as a weakly temperature-dependent adjustable parameter. Traditionally the universal curve is represented by a polynomial expansion in reduced density that for extended hard-sphere model takes the form,

$$\log_{10}(1 + \Delta\eta^*) = \frac{6.26871}{V^*} - \frac{48.4793}{(V^*)^2} + \frac{243.447}{(V^*)^3} - \frac{653.257}{(V^*)^4} + \frac{974.312}{(V^*)^5} - \frac{763.616}{(V^*)^6} + \frac{251.193}{(V^*)^7}.$$

(2)

The universal curve is valid in an extended range of reduced volumes ($V^* \geq 1.19$) and the coefficients were determined by fitting to high-quality experimental viscosity data [24]. Although the universal curve extends to higher density and can be safely extrapolated to lower density, it is nearly indistinguishable from the original DA correlation [14] in its range of validity at the liquid-like densities, that corresponds to $1.5 \leq V^* \leq 2.5$ in the reduced volume.

For n -alkanes the molar core volumes are represented by the following empirical correlations in terms of T and carbon number n

for methane to n -butane,

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = 45.822 - 6.1867\theta^{1/2} + 0.36879\theta - 0.007273 \theta^{3/2} + n(2.17871 \theta^{1/2} - 0.185198\theta + 0.00400369\theta^{3/2}) + n^2(6.95148 - 52.6436\theta^{-1/2}) + n^3(-7.801897 + 42.24493\theta^{-1/2} + 0.4476523\theta^{1/2} - 0.009573512\theta) \quad (3)$$

for n -pentane,

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = 81.1713 - 0.046169\theta \quad (4)$$

and for n -hexane to n -hexadecane,

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = 117.874 + 0.15(-1)^n - 0.25275\theta + 0.000548\theta^2 - 4.246 \times 10^{-7} \theta^3 + (n-6)(1.27 - 0.0009\theta)(13.27 + 0.025n) \quad (5)$$

where $\theta = T/K$. The expressions were originally proposed by Assael et al. [14] based on the analysis of the primary transport property data on liquid n -alkanes. The temperature range of correlations for core molar volume, Eqs (3) to (5) is limited to $110 \leq T/K \leq 400$. The use of these correlations in the extended hard-sphere model ensures that for the first sixteen n -alkanes the predictions of the model are compatible to those of the DA hard-sphere model. Finally the expression used for the roughness factor of n -alkanes, R_η , that enters the definition of the reduced excess viscosity, Eq. (1) is given by [14]

$$R_{\eta} = 0.995 - 0.0008944n + 0.005427n^2. \quad (6)$$

The set of Eqs (1-6) represent the extended hard-sphere model that can be used to evaluate the viscosity of the first sixteen n -alkanes at any temperature and density of interest within the range of validity, providing zero-density viscosity value is available. The model is capable of representing experimental viscosity data within $\pm 5\%$. As with most methods for predicting viscosity, the extended hard-sphere model presented here is very sensitive to density and an accurate equation of state is needed if density is to be determined from specified values of temperature and pressure.

Ciotta et al. [24] have extended the analysis of n -alkane viscosity data to include n -octadecane and have re-evaluated n -hexadecane. In the process they have proposed separate correlations for the core molar volume and provided values of roughness factor R_{η} for these two n -alkanes. As we have already discussed in the introduction the extent of the available data on long-chain alkanes is not sufficient to carry out a full analysis for other fluids. Hence in this work we have used the model summarized by Eqs. (1) to (6) in a predictive mode using only R_{η} as an adjustable parameter. In order to do so we had supplemented the extended hard-sphere model with a model to estimate the viscosity of the long-chain n -alkanes in the zero-density limit.

2.2 The zero-density viscosity

As the number of carbon atoms in the alkane chain increases, the zero density viscosity decreases and so does its contribution to the overall viscosity, especially at high density. Hence, in principle any of the available methods [25] for estimating zero-density viscosity should suffice. However, in practice the use of viscosity of pure species to predict the viscosity of mixtures, for instance in VW model [20-23], places a greater emphasis on getting the accurate values of zero-density viscosity. The difficulty of obtaining accurate values by

experimental means increases with increasing number of carbon atoms, as at a given temperature one would need to perform the measurements at ever decreasing vapour pressures. Hence, there is a greater need for theoretically based predictive models that ensure correct extrapolation with increasing chain length of n -alkane.

In the present work the viscosity in the zero-density limit $\eta_0(T)$ has been represented by means of a standard relationship in kinetic theory [26], that in practical engineering form is given by,

$$\eta_0/(\mu Pa.s) = 0.083867\sqrt{MT} \frac{f_\eta}{\Omega_\eta} \quad (7)$$

where Ω_η is the viscosity collision integral and f_η is the higher-order correction factor that for all the systems studied so far [26-30] is within a few percent of unity. There are a number of ways of calculating the collision integral [25,26]. In this work we have, for reasons of simplicity and continuity with previous work [24,31], opted to use the collision integral that arises from the effective spherical Lennard-Jones (12-6) potential in conjunction with Kihara second-order expression for the higher order correction factor [26]. Both quantities can be expressed in terms of empirical relationships [32] in reduced temperature,

$$\Omega_\eta = \pi\sigma^2\Omega_\eta^* \quad (8)$$

$$\Omega_\eta^* = 1.16145T^{*-0.14874} + 0.52487 \exp(-0.7732T^*) + 2.16178 \exp(-2.43787T^*) - 6.435 \times 10^{-4} T^{*0.14874} \sin(18.0323 T^{*-0.76830} - 7.27371) \quad (9)$$

$$f_\eta = 1 + \frac{3}{49}(4E^* - 3.5)^2 \quad (10)$$

$$E^* = [1.11521T^{*-0.14796} + 0.44844 \exp(-0.99548T^*) + 2.30009 \exp(-3.06031T^*) + 4.565 \times 10^{-4} T^{*0.14796} \sin(38.5868 T^{*-0.69403} - 2.56375)] / \Omega_\eta^* \quad (11)$$

$$T^* = T/\varepsilon \quad (12)$$

where T^* is the reduced temperature and ε and σ are the energy and length scaling parameters in units of K and nm, respectively. The Eqs. (7) to (12) can be used to calculate the zero-density viscosity at any temperature of interest provided the values of the scaling parameters ε and σ for a given n -alkane are known.

3. Results and Discussion

In order to extend the model to long-chain n -alkanes we need to develop a methodology for predicting the core molar volume, V_0 , the roughness factor R_n and the zero-density scaling parameters ε and σ for each alkane. We first investigate the zero-density viscosity.

3.1 The zero-density viscosity

Traditionally the values of scaling parameters ε and σ are obtained, for each fluid, by fitting Eqs. (7) to (12) to accurate values of zero-density viscosity. For short-chain n -alkanes, where the viscosity data exist, such a procedure leads to reliable results. However, for long-chain alkanes there are no viscosity data and we have to rely on estimating the scaling parameters by extrapolating the values obtained for short-chain n -alkanes.

For nine n -alkanes (methane to n -butane, n -hexane to n -octane, n -decane and n -dodecane) there exist reliable correlations of the zero-density viscosity [12, 4-10], with well-defined uncertainty limits, based on the critical assessment of the available experimental data. For the purposes of this work we used these correlations summarized in Table 1, within their temperature range, as the primary data. We have also included, in the primary data set, the zero-density viscosity values for n -pentane obtained by Vogel and Holdt from their measurements of viscosity of n -pentane at low density [33].

TABLE 1. Evaluation of the zero-density viscosity correlation
against the primary experimental data.

n-alkane	T range (K)	AAD (%)	MD (%)
methane [12]	80 - 1500	0.8	1.6
ethane [4]	212 - 625	0.7	2.4
propane [5]	293 - 625	0.5	0.7
<i>n</i> -butane [6]	293 - 600	0.3	1.1
<i>n</i> -pentane [33]	323 - 633	0.5	0.7
<i>n</i> -hexane [7]	298 - 631	0.9	1.2
<i>n</i> -heptane [8]	317 - 632	1.3	1.7
<i>n</i> -octane [9]	380 - 687	1.0	1.8
<i>n</i> -decane [9]	446 - 709	1.9	2.4
<i>n</i> -dodecane [10]	503 - 681	0.8	1.9
Entire Data set		0.9	2.4

$$\text{AAD} = 100/N \sum |(\eta_{\text{exp}} - \eta_{\text{corr}})/\eta_{\text{exp}}|;$$

Figure 1 illustrates the results for methane where we made use of the recommended data by Hellmann et al. [12] that covers a wide temperature range, $80 < T/K < 1500$ and that has uncertainty of 0.5 % around room temperature, increasing to 1.0 % at both low and high temperature limits. We have scaled these data by multiplying the calculated values by 0.9955, as recommended by Hellmann [34] to bring them in line with the best available experimental data.

Fig. 1. Maximum percentage deviation of the calculated zero-density viscosity for methane from the Hellmann et al. [12] values multiplied by a factor of 0.9955, as explained in the text, for different values of the Lennard-Jones energy and length scaling parameters, ϵ and σ .

We observe that the effective spherical Lennard-Jones potential can only represent the data at the 1.6 % level of uncertainty. Although this is outside the claimed uncertainty of the data it is sufficient for the purposes of estimating the scaling parameters of long-chain alkanes. Furthermore, we observe in Figure 1, that there is a wide range of ϵ and σ values that would fit the viscosity data with the same overall deviation. This feature has two consequences. It makes fitting scaling parameters a notoriously difficult [25] problem for gradient-descent algorithms, because the solution is located on a very flat minimum. For this reason, we fitted the scaling parameters for methane by global search in the solution space, thus ensuring that the absolute minimum is located. Secondly, it makes it difficult to establish trends in both scaling parameters as a function of increasing carbon number, n . In order to resolve this issue we have constrained the values of σ for other n -alkanes by using a semi-empirical relationship,

$$\sigma_n = \sigma_{CH_4} \sqrt{1 + (n - 1)/3} \quad (13)$$

The relationship is based on the argument put forward by Galliero and Boned [31] that for a chain consisting of n_s hard-sphere segments of diameter, σ_s , the mean square of the end-to-end vector $\mathbf{R}$ is such that $\langle \mathbf{R}^2 \rangle = n_s \sigma_s^2$. If we assume, that the chain can be represented by a single hard-sphere of an effective diameter σ_{hs} we end up with a relationship $\sigma_{hs} = \sqrt{n_s} \sigma_s$. If we further base the diameter of a single segment on the diameter of a methane molecule, then the number of segments needed to represent n -alkane is related to the number of carbon atoms by an expression previously used in the description of the critical properties [35], SAFT-EOS [36] and viscosity of dense fluids [22], namely $n_s = 1 + (n - 1)/3$. In this work we have assumed that the resulting relationship will be a good approximation for the Lennard-Jones length scaling parameters σ , Eq. (13).

Constraining the value of the length scaling parameter, σ , allowed for the unique determination of the energy scaling parameter, ε , for each n -alkane, by means of a fitting to experimental viscosity data. The resulting values displayed monotonic increase with the number of carbon atoms that indicated converging behaviour for very long chains. Although there is theoretical evidence [35] that the critical temperature of chain molecules converges to a limit with increasing chain length, and some authors [37] have imposed such a limit when developing empirical correlations, the most recent work [38] has argued that there is not enough experimental data to estimate the limit correctly. As there was no other observation that could be used to guide the choice of the functional form, the values of the energy scaling parameter ε were fitted to empirical correlation of the form

$$\varepsilon_n = \varepsilon_{CH_4} + A (\ln n)^B \quad (14)$$

where A and B are adjustable parameters. The fitted parameters A , B , ϵ_{CH_4} and σ_{CH_4} , to be used in the representation of zero-density viscosity, are given in Table 2. Table 1 summarizes the absolute average deviation (AAD) and the maximum average deviation (MD) between the recommended data and the zero-density viscosity data calculated by means of Eqs (7) to (12) for ten fluids used in the fitting procedure.

TABLE 2 Coefficients for the representation of the zero-density viscosity,
Eqs. (7) - (14)

A	143.6 K
B	0.833
ϵ_{CH_4}	148.2 K
σ_{CH_4}	0.3754 nm

Figure 2 illustrates the behaviour of the zero-density viscosity at 373.15 K generated by the model developed in this work. It exhibits monotonic decrease, with increasing carbon number of n -alkane, at all temperatures of interest. For comparison we have also calculated the zero-density viscosity using the recommended empirical correlations by Lucas [25, 39] and Chung [25, 40] and the method suggested by Ciotta et al. [24]. Lucas method is based on a corresponding states expression that relates the reduced zero-density viscosity to an universal function in terms of reduced temperature, while the method of Chung uses, for non-polar gases, the expressions for the zero-density viscosity given by Eq. (7) with the collision integral given by Eq. (8) and the higher-order correction factor replaced by an empirical expression in terms of the acentric factor. The scaling parameters ϵ and σ are calculated from the critical temperature and critical volume, respectively by means of the empirical expressions [25]. The longest n -alkane molecule used in the development of the correlations was n -pentane. For n -alkanes longer than octane Ciotta et al. [24] also made use of Eq. (7), neglecting the higher-order correction factor, but used Vicharelli's [41]

analytical approximation for the Lennard–Jones(12,6) collision integrals and different empirical expression for ε and σ [42] in terms of the critical temperature and pressure. None of the correlations were designed to give accurate zero-density viscosity values for long chain n -alkanes. The lack of input viscosity data and the empirical relationships between the scaling parameters and critical properties, which at best are rough approximations [25, 42], preclude that.

Figure 2 illustrates that Lucas and Ciotta et al. methods exhibit unexpected behaviour when extrapolated beyond $n=37$, while the viscosity calculated by Chung's method [25, 39] exhibit the expected monotonic decrease with an increase in a number of carbon atoms. Initial calculations of viscosity of mixtures containing long n -alkane species using the VW method [20-23] indicate that Chung's method underestimate η_0 of long chain n -alkanes [43]. We have also compared how the three methods predict the best available viscosity data on n -alkanes, as summarized in Table 1. The AAD of the entire set as predicted by Lucas's [25, 39], Chung's [25, 40] and Ciotta et al. [24] methods is 2.2 %, 2.1 % and 2.8 %, respectively, while the maximum deviations are 4.5 %, 6.0 % and 8.3 %. This further supports that the present method is more accurate, than what is currently available.

Fig. 2. The behaviour of the zero-density viscosity calculated at 373.15 K as a function of the number of carbon atoms using four different methods: (—) current method; (- - -) Chung method [25,40]; (- · - · -) Ciotta et al. method [24]; (· · · ·) Lucas method [25,39].

3.2 The viscosity at high density

As has been previously stated [24] Ciotta et al. model, like most viscosity models, is sensitive to the value of density used. Hence in order to develop a reliable viscosity correlation, it is essential to make use of viscosity-density data of low uncertainty. The lack of a reliable density prediction method for long chain *n*-alkanes led us to limit our consideration only to *n*-alkanes where densities are reported alongside the viscosity. A literature search indicates that the measurements of viscosity of long-chain *n*-alkanes are scarce and only 15 datasets could be used in the development of the correlation. Table 3 summarizes the available data [44-51] detailing the technique employed to perform the measurements, the temperature and pressure ranges and the authors' claimed uncertainty. The viscosity data cover a wide range of temperature, but only one set of data [45] reports the measurements at pressures higher than atmospheric. The measurements of the viscosity of liquid *n*-alkanes reported in Table 3 were performed in a variety of viscometers. Although the capillary and vibrating wire viscometers are considered to be primary instruments, as the full working equations are available, the measurements by means of the rolling ball viscometer can produce values with larger than anticipated uncertainty. The analysis of measurements by Queimada et al. [48] for pure *n*-heptane, *n*-decane and *n*-hexadecane, carried out in the rolling ball viscometer indicates that the AAD from the recommended correlations [8,9,24] is 2.5 %, 3.1 % and 1.0 %, respectively, although the maximum deviation reaches 5.1 %. Based on this comparison the viscosity values obtained in the rolling ball viscometers were assigned an uncertainty of approximately 2-4 %. Only for two alkanes were the measurements reported by more than a single laboratory. The viscosity of icosane (*n*-C₂₀H₄₂) has been measured by three different authors [47-49], while the viscosity of tetracosane (*n*-C₂₄H₅₀) has been measured by two investigators [48,50], in

the overlapping temperature range at atmospheric pressure. The data on icosane agrees within ± 1.5 % with each other, while for tetracosane we observe a systematic difference of approximately 5 %, with the viscosity data of Queimada et al. [48] being lower than that measured by Wakefield et al. [50].

As the data for each fluid are insufficient to obtain reliable values of the closed-packed volume V_0 , we have extrapolated the existing correlation for V_0 , Eqs (3-5) to higher carbon numbers ($n < 64$) and performed a fitting to experimental viscosity data by using the roughness parameter R_η as an adjustable fluid-dependent parameter. As we employed the expressions for V_0 given by eqs. (3-5), the upper temperature limit for each n -alkane was 400 K. Table 3 summarizes how many viscosity data points were used to fit R_η for each fluid.

TABLE 3. Primary data used in developing the viscosity correlation

Authors	n	Technique employed ^a	Claimed uncertainty (%)	Pressure range (MPa)	Temperature range (K)	No. of data	No. of data used
Doolittle and Peterson [44]	17	C	0.8	0.1	295-574	8	4
Caudwell et al. [45]	18	VW	2.0	0.1-92	323-473	49	21
Chu et al. [46]	19	C	-	0.1	308-343	8	8
Ototake [47]	20	-	-	0.1	313-613	31	9
Queimada et al. [48]	20	RB	-	0.1	313-343	4	4
Schiessler and Whitmore [49]	20	C	-	0.1	311-372	3	3
Queimada et al. [48]	22	RB	-	0.1	323-343	3	3
Queimada et al. [48]	24	RB	-	0.1	333-343	2	2
Wakefield et al. [50]	24	C	0.5	0.1	328-338	2	2
Doolittle and Peterson [44]	28	C	1.5	0.1	335-574	6	2
Aasen et al. [51]	32	RB	1.5	0.3	373-466	8	3
Doolittle and Peterson [44]	36	C	1.5	0.1	373-574	5	1
Aasen et al. [51]	44	RB	1.5	0.3	369-474	5	2
Aasen et al. [51]	60	RB	1.5	0.3	392-466	5	1
Doolittle and Peterson [44]	64	C	1.6	0.1	383-574	5	1

^aC, capillary; RB, rolling ball; VW, vibrating wire.

Figure 3 illustrates the roughness factor, R_η , obtained by fitting the available viscosity data for each n -alkane ($17 < n < 64$) to the extended hard-sphere model, as used in this work. The trend with carbon number is essentially linear up to $n=44$ and then we observe departure from linearity. It should be noted however, that the estimation of the roughness factor for n -alkanes with more than 32 carbon atoms was based on fitting to just a single viscosity datum for each fluid. Furthermore, the two values of viscosity used to determine the roughness factor for $n \geq 60$ were in the range 10-15 mPa·s and are much larger than viscosity values of n -alkanes used to generate Eq. (5). Hence the resulting values of R_η exhibit a high level of uncertainty.

The values of roughness factor were correlated by a simple expression,

$$R_\eta = 2.6380 + 0.157(n - 18) \quad n \geq 17 \quad (15)$$

Fig. 3. The roughness factor, R_η , as a function of carbon number, n : (•) fitted values; (—) Eq. (6); (---) Eq. (15)

Figure 4 illustrates the relative percentage deviation of the measured data for n -alkanes up to and including tetratetracontane ($n\text{-C}_{44}\text{H}_{90}$) from the values calculated by the model developed in this work, up to 400 K, which is the range of validity of expression for V_0 , Eq. (5). The relative deviations are within 5.0 % with the exception of a single point measured by Chu et al. [46] for nonadecane ($n\text{-C}_{19}\text{H}_{40}$), the viscosity data for tetracosane ($n\text{-C}_{24}\text{H}_{50}$) measured by Queimada and co-workers [48] and the high pressure data ($P > 42$ MPa) of Caudwell et al. [45]. The data of Queimada and co-workers for other fluids studied in this work ($n\text{-C}_{20}\text{H}_{42}$ and $n\text{-C}_{22}\text{H}_{46}$) are reproduced with the maximum deviation of 2.5 %, while as discussed previously the data for shorter chain alkanes ($n\text{-C}_7\text{H}_{16}$, $n\text{-C}_{10}\text{H}_{22}$ and $n\text{-C}_{16}\text{H}_{34}$) are reproduced within the overall AAD of 2.2 % and the maximum deviation of 5.1 %, so it is not too surprising to observe under prediction of 6.6 % to 6.9 % for $n\text{-C}_{24}\text{H}_{50}$. An indication that the uncertainty of these measurements might be higher than for other

Fig. 4. Relative percentage deviations, $[100(\eta_{\text{model}} - \eta_{\text{exp}})/\eta_{\text{exp}}]$, of the values calculated by the present model from the experimental viscosity data, at temperatures below 400 K: (o) $n\text{-C}_{17}\text{H}_{36}$ [44]; (●) $n\text{-C}_{18}\text{H}_{38}$ [45]; (Δ) $n\text{-C}_{19}\text{H}_{40}$ [46]; ($\blacktriangle$) $n\text{-C}_{20}\text{H}_{42}$ [47]; ($\blacktriangledown$) $n\text{-C}_{20}\text{H}_{42}$ [48]; ($\blacklozenge$) $n\text{-C}_{20}\text{H}_{42}$ [49]; ($\blacksquare$) $n\text{-C}_{22}\text{H}_{46}$ [48]; ($\blacklozenge$) $n\text{-C}_{24}\text{H}_{50}$ [48]; ($\blacklozenge$) $n\text{-C}_{24}\text{H}_{50}$ [50]; ($\star$) $n\text{-C}_{28}\text{H}_{58}$ [44]; ($\diamond$) $n\text{-C}_{32}\text{H}_{66}$ [51]; ($\square$) $n\text{-C}_{36}\text{H}_{74}$ [44]; (∇) $n\text{-C}_{44}\text{H}_{90}$ [51];

alkanes is provided by the good agreement of the model with the data of Wakefeld and co-workers [50], who also measured the viscosity of tetracosane but in a capillary viscometer, and whose data is reproduced within 1-2 %. The four high pressure data points ($P > 42$ MPa) of Caudwell et al. at high temperature ($T > 373$ K) are also reproduced with deviations larger than 5 %, with maximum deviation of 8.5 %. Similar deviations were reported by Ciotta [24] for Caudwell et al. high-pressure, high-temperature data of dodecane. This is a direct result of using the general expression for V_0 , Eq. (5), beyond its range of validity in terms of carbon number. We note that if V_0 is fitted to octadecane data alone, the Caudwell et al. data can be reproduced with the maximum deviation of 3.8 % [24]. This indicates that further refinement of the general expression for V_0 , Eq. (5) is necessary to reconcile high-pressure, high-temperature data. Such a modification can be only made when and if accurate and plentiful high-pressure, high-temperature data for n -alkanes longer than octadecane becomes available.

Finally, the data points pertaining to $n\text{-C}_{60}\text{H}_{122}$ and $n\text{-C}_{64}\text{H}_{130}$, not shown in Figure 5, are reproduced with relative deviation of 19.5 % and 31.4 %, respectively. Notwithstanding that for such relatively high viscosities for n -alkanes ($\eta \sim 10\text{-}15$ mPa.s), the sensitivity to density is pronounced; a 0.5% change in density will result in approximately 8-10 % change in viscosity. This most likely indicates that the carbon number limit of extrapolation of the expression for V_0 , Eq. (5), has been reached.

It is interesting to note that if we extrapolate the expression for V_0 , Eq. (5), to higher temperature the uncertainty of the proposed scheme does not deteriorate and the deviations are by and large within 5 % bounds, as illustrated in Fig. 5. The exceptions are the high pressure data for $n\text{-C}_{18}\text{H}_{38}$ of Caudwell et al. ($P > 30$ MPa) and the data for n -alkanes composed of 44 or more carbon atoms. For completeness we have summarized the deviations of the calculated viscosity values from the experimental ones in Table 4.

Hence, the present scheme for longer n -alkanes compares favourably with the original [14] and the extended scheme [24] which also claim to represent the data within 5 %. A further refinement of the scheme is possible, but would require the availability of experimental data,

for alkanes consisting of more than eighteen carbon atoms, covering pressures higher than atmospheric. When such data become available it would be possible to refine the expressions for V_0 and R_η further, rather than rely on extrapolation to carbon number higher than 18 and temperatures higher than 400 K.

Fig. 5. Relative percentage deviations, $[100(\eta_{\text{model}} - \eta_{\text{exp}})/\eta_{\text{exp}}]$, of the values calculated by the present model from the experimental viscosity data at temperatures above 400 K: (o) $n\text{-C}_{17}\text{H}_{36}$ [44]; (●) $n\text{-C}_{18}\text{H}_{38}$ [45]; (▲) $n\text{-C}_{20}\text{H}_{42}$ [47]; (★) $n\text{-C}_{28}\text{H}_{58}$ [44]; (◇) $n\text{-C}_{32}\text{H}_{66}$ [51]; (□) $n\text{-C}_{36}\text{H}_{74}$ [44]; (▽) $n\text{-C}_{44}\text{H}_{90}$ [51]; (+) $n\text{-C}_{60}\text{H}_{122}$ [51]; (x) $n\text{-C}_{64}\text{H}_{130}$ [44];

TABLE 4. Evaluation of the viscosity correlation against the experimental data

Authors	<i>n</i>	<i>T</i> < 400 K			<i>T</i> > 400 K		
		No. of data	AAD (%)	MD (%)	No. of data	AAD (%)	MD (%)
Doolittle and Peterson [44]	17	4	3.2	-4.6	4	1.4	2.3
Caudwell et al. [45] ^a	18	14	2.0	3.9	-	-	-
Caudwell et al. [45] ^b	18	7	1.8	-4.3	9	2.9	4.3
Caudwell et al. [45] ^c	18	7	6.2	-8.5	12	8.4	-12.9
Chu et al. [46]	19	8	2.4	5.9	-	-	-
Ototake [47]	20	9	1.0	2.6	22	2.7	5.1
Queimada et al. [48]	20	4	1.7	2.6	-	-	-
Schiessler and Whitmore [49]	20	3	0.7	1.0	-	-	-
Queimada et al. [48]	22	3	0.8	0.9	-	-	-
Queimada et al. [48]	24	2	6.8	-6.9	-	-	-
Wakefield et al. [50]	24	2	1.9	-2.5	-	-	-
Doolittle and Peterson [44]	28	2	1.3	-2.1	4	1.9	-2.9
Aasen et al. [51]	32	4	1.4	-2.0	4	3.1	-3.5
Doolittle and Peterson [44]	36	1	0.4	-0.4	4	4.8	-8.4
Aasen et al. [51]	44	2	2.2	3.0	3	6.9	-8.4
Aasen et al. [51]	60	1	19.5	19.5	3	5.6	11.1
Doolittle and Peterson [44]	64	1	31.4	31.4	4	11.0	-15.4

^adata below 373 K; ^bdata above 373 K and below 30 MPa; ^cdata above 373 K and 30 MPa,

Table 5 is provided to assist the user in computer-program verification. The viscosity calculations are based on the tabulated temperatures and densities and the molar mass of each *n*-alkane was calculated using atomic masses of 12.0107 and 1.00794 for C and H atoms, respectively.

TABLE 5. Sample points for computer verification of the correlating equations

n	T (K)	ρ (kg.m ⁻³)	η (μPa.s)
1	200	0.0	7.801
1	1000	0.0	27.545
4	300	0.0	7.394
12	500	0.0	7.806
16	500	0.0	6.781
18	373	700.0	839.40
18	500	780.0	1138.08
24	373	780.0	3356.83
24	373	800.0	4738.10
44	474	720.0	1836.48

4. Conclusions

An extended hard-sphere model was used as the basis for developing the model to predict the viscosity of pure, long-chain *n*-alkanes. In order to properly account for the behaviour at dilute gas limit, a new zero-density viscosity model was developed and incorporated into the extended hard-sphere model. It assumes that the molecular interactions can be described by an effective Lennard-Jones 12-6 potential, where the scaling parameters, for each *n*-alkane, are obtained from those of methane. The length scaling parameter is based on a semi-empirical relationship that has its foundations in the analysis of interaction of chains consisting of hard-sphere segments, while the energy scaling parameter is obtained by means of two-parameter empirical relationship. The resulting model predicts the zero-density viscosity within 2.4%, based on a comparison with reliable and accurate experimental viscosity data. The uncertainty of the predicted values is better than currently available.

In order to adapt the extended hard-sphere model to longer alkanes, the present model retains the correlations of molar core volume, V_0 , developed in earlier work for *n*-alkanes smaller than hexadecane and it makes use of the roughness factor, R_η as a single fitting parameter for each *n*-alkane. The advantage is taken of the linear behaviour of the roughness factor as a function of number of carbon atoms to propose a simple empirical relationship. The resulting model reproduces the available experimental viscosity data on long chain *n*-alkanes up to tetracontane ($n\text{-C}_{44}\text{H}_{90}$) within $\pm 5\%$ at atmospheric pressure. However, at temperatures higher than 400 K, where the expression for V_0 is extrapolated, the evidence is based on a very limited set of data and would require further corroboration. At higher pressures and for longer *n*-alkanes the performance deteriorates, indicated that the more reliable extrapolation of the original $V_0(T)$ parameter needs to be developed. Such a development would require additional experimental data. As with the original DA approach and the extended hard-sphere model, the method developed here is very sensitive to density, especially at densities where viscosity increases rapidly. The model thus requires an

accurate equation of state, if density is to be determined from specified values of temperature and pressure.

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