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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-$C_{40}H_{82}$) 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.

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) there exist accurate and reliable correlations of viscosity that cover a wide range of temperatures and pressures, with well-defined estimates of uncertainty [3–10]. 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

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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 ±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],

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

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 cm^3 mol^{-1} and μPa.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,

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

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,

$$V_0\Big/\left(\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\right) = 45.822 - 6.1867\theta^{1/2} + 0.368790\theta - 0.007273\theta^{3/2} + n\left(2.17871\theta^{1/2} - 0.185198\theta + 0.00400369\theta^{3/2}\right) + n^2\left(6.95148 - 52.6436\theta^{-1/2}\right) + n^3\left(-7.801897 + 42.24493\theta^{-1/2} + 0.4476523\theta^{1/2} - 0.009573512\theta\right), \tag{3}$$

for *n*-pentane,

$$V_0\Big/\left(\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\right) = 81.1713 - 0.046169\theta, \tag{4}$$

and for *n*-hexane to *n*-hexadecane,

$$V_0\Big/\left(\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\right) = 117.874 + 0.15(-1)^n - 0.25275\theta + 0.000548\theta^2 - 4.246\times10^{-7}\theta^3 + (n-6)(1.27 - 0.0009\theta)(13.27 + 0.025n), \tag{5}$$

where $\theta = T/\mathrm{K}$. The expressions were originally proposed by Assael et al. [14] based on the analysis of the primary transport property