Extended hard-sphere model for the viscosity of dense fluids

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ABSTRACT

An extended hard-sphere model is reported that may be applied to correlate and predict the viscosity of gases, liquids and supercritical fluids. The method is based on the hard-sphere model of Dymond and Assael and uses their roughness factors and molar core volumes to relate reduced viscosity to a universal function of reduced volume. The extended model behaves correctly in the limit of low densities and offers improved accuracy at high densities. The new universal reference function was determined from a large database of experimental viscosities for alkanes extending up to reduced densities of 0.84. It has been tested by correlating the viscosity of two high-viscosity liquids not used in the development of the universal function and has shown to perform satisfactorily up to reduced densities of approximately 0.9.

1. Introduction

Viscosity is an important transport property from a technological point of view and plays an essential part in the calculation of fluid flow through conduits of all kinds. There is a strong economic case for developing the means to estimate viscosity accurately and reliably. For a number of simple pure fluids correlations of critically evaluated experimental data are available. However, relying on experimental means alone is not sufficient. For engineering purposes, models are required that can predict the viscosity of fluids, including mixtures, as a function of temperature, pressure and composition. Thus one needs to develop generic predictive models that have some basis in the underlying physical theory and that are valid for a plethora of different fluids at different conditions.

This requirement can be satisfied rigorously only for gases at low densities, where kinetic theory provides the necessary link between molecular and transport properties and the Chapman–Enskog solution of the Boltzmann equation is valid [1]. Under such conditions, it is possible to predict accurately the viscosity of a number of simple gases with an accuracy that is commensurate with the best experimental data [2–6]. No rigorous and complete theory exists for dense fluids, as the general solution of the Boltzmann equation is not available. The only tractable solutions developed to date are based on assuming that the molecules interact as hard spheres and that their collisions are uncorrelated. The resulting Enskog equation 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 [7–11] and the Vesovic–Wakeham (VW) model [12–16]. Underlying these approaches is the idea that the transport properties of real dense fluids are dominated by repulsive interactions between molecules and may be related to those of an equivalent hard-sphere fluid. The Enskog equation features in these models as an approximation for the viscosity of the equivalent hard-sphere fluid, and the two models differ in the way that they address the limitations of this equation. The present work is related to the DA approach and had the objective of extending the range of densities over which that method may be applied reliably in the correlation of viscosity for pure fluids. This work is however also related to the VW approach in the following way. The VW approach, in its simplest form [12–14], seeks to relate the viscosity of an arbitrary mixture to the viscosity of each individual component at the temperature and molar volume of interest and, for that purpose, accurate correlations of pure-fluid viscosities are required. A current limitation of the VW model can be traced to the lack of correlative models that apply at very high densities which the present extension of the DA model will help address. More generally, the DA approach can be useful as a predictive tool for mixtures in its own right, at least for those containing molecules from within a single homologous series [9].

In the remainder of this article we first detail the original DA approach for the correlation of pure-fluid viscosity; we then

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introduce an extended hard-sphere model based on the excess viscosity as a means of ensuring correct behaviour in the limit of low density; finally we describe the development and testing of a new universal reference function for excess viscosity.

2. The hard-sphere model

The hard-sphere model for the transport properties of dense fluids was proposed by Dymond [17,18], and refined into a practical predictive tool by Dymond, Assael and their collaborators [7–11]. In the smooth-hard-sphere model, all thermodynamic and transport properties are athermal and may be conveniently expressed as functions of the reduced volume $V^* = V_m/V_0$, where V_m is the molar volume, $V_0 = N_A\sigma^3/\sqrt{2}$ is the molar volume for close-packed hard spheres, N_A is Avagadro's constant and σ is the diameter of the molecules. It is also convenient to work in terms of reduced transport coefficients and in the DA approach, the reduced viscosity η^* was defined as follows:

$$\eta* = \left(\frac{\eta}{\eta_0}\right)\left(\frac{V_m}{V_0}\right)^{\frac{2}{3}}, \tag{1}$$

where η_0 is the viscosity of the same system in the dilute-gas limit. Neglecting higher-order correction factors, $\eta_0 = (5/16\sigma^2)(mk_BT/\pi)^{1/2}$, where m is the mass of one molecule, and k_B is Boltzmann's constant. Thus the full expression for η^* is

$$\eta* = \left(\frac{16}{5}\right)(2N_A)^{\frac{1}{3}}\left(\frac{\pi}{MRT}\right)^{\frac{1}{2}}V_m^{\frac{2}{3}}\eta, \tag{2}$$

where M is the molar mass and R the gas constant. In principle, the reduced viscosity η^* of smooth hard spheres can be determined as a function of V^* by molecular simulation. Indeed, the approach initially used to determine $\eta^*(V^*)$ was to combine the Enskog approximation for the viscosity of smooth hard spheres with a correction derived from molecular dynamics calculations [17].

To apply the smooth hard sphere model to systems of real spherical molecules, it is noted that, at sufficiently high densities, the thermophysical properties of liquids and supercritical fluids are dominated by repulsive interactions and can be mapped approximately on to those of the hard-sphere model if the reducing volume V_0 is treated as a weakly temperature-dependent parameter. Thus, having established the universal function $\eta^*(V^*)$ from simulation and theory, the viscosity of a simple molecular fluid could be correlated along an isotherm by selecting an optimal value of V_0 for that molecule at a given temperature. Considering a range of temperatures, the substance-dependent molar core volume V_0 was found to decrease slowly with increasing T. For practical purposes, $V_0(T)$ is usually approximated by a simple polynomial in T [7,19].

It was found that the hard-sphere model could also be applied successfully to non-spherical molecules by treating them as rough-hard-spheres, for which the expression for viscosity is modified by a simple multiplicative parameter, usually taken to be temperature independent. Thus, a more general expression for the reduced viscosity is

$$\eta* = \left(\frac{16}{5}\right)(2N_A)^{\frac{1}{3}}\left(\frac{\pi}{MRT}\right)^{\frac{1}{2}}V_m^{\frac{2}{3}}\left(\frac{\eta}{R_\eta}\right), \tag{3}$$

where R_η is called the roughness factor [9]. To correlate the experimental viscosity surface $\eta(T,V_m)$ of a substance, it is therefore necessary to determine the constant R_η and the parameters of $V_0(T)$ that best map the experimental reduced viscosity η^*, defined by Eq. (3), onto the universal function $\eta^*(V^*)$ for smooth hard spheres.

One limitation of the method as originally formulated was that the universal function $\eta^*(V^*)$ for smooth-hard-spheres was subject to significant computational uncertainties at high densities, especially above the equilibrium freezing density. Thus, in later work, $\eta^*(V^*)$ was parameterised by considering the experimental data for normal alkanes; this led to a representation of $\eta^*(V^*)$ by an eight-term polynomial in $(1/V^*)$ valid in the interval $1.5 \le V^* \le 5$, corresponding to the normal liquid range of many substances [7]. Recent molecular dynamics calculations for smooth hard spheres provide much improved results [20–22] which we considered further below.

The original hard-sphere scheme for viscosity is successful within its range of applicability, often representing experimental data within ±5%. The method was also applied to the thermal conductivity and self-diffusion coefficients for which further universal reference functions are defined [7]. The same molar core-volume function $V_0(T)$ is used for all three properties of a given substance, although different roughness factors apply for viscosity, thermal conductivity and self diffusion. It is important to note that the method is very sensitive to the values of molar volume used, with relative errors in V_m typically leading at high densities to relative errors in η approximately one order of magnitude greater. Thus, when interpreting experimental data at given temperature and pressure, one requires precise knowledge of the corresponding molar volume.

2.1. The extended hard-sphere model

As noted above, the hard-sphere scheme was restricted to reduced volumes in the range $1.5 \le V^* \le 5$. Outside this interval, the scheme breaks down; it diverges in the approach to the dilute gas limit, and also exhibits strong deviations with respect to experimental data at high reduced densities. To address the first of these deficiencies, Caudwell [23] proposed the use of an excess reduced viscosity, defined as

$$\Delta\eta* = \frac{16}{5}(2N_A)^{\frac{1}{3}}\left(\frac{\pi}{MRT}\right)^{\frac{1}{2}}V_m^{\frac{2}{3}}\left(\frac{\eta - \eta_0}{R_\eta}\right), \tag{4}$$

which has the property that $\Delta\eta^* \to 0$ in the dilute gas limit where $\eta \to \eta_0$. This ensures that the model behaves reasonably at low densities. Since in the dense fluid region $\eta >> \eta_0$, the excess reduced viscosity $\Delta\eta^*$ does not differ significantly from η^* and the two are essentially identical at high densities. Thus, Caudwell was able to construct a new universal curve, $\Delta\eta^*(V^*)$, by simply matching it to the original DA correlation for η^* over the range $1.25 \le V^* \le 2.5$. No data were fitted in the low-density region $V^* > 2.5$ and the correlation were simply constrained such that $\Delta\eta^* \to 0$ as $1/V^* \to \infty$ by means of the following polynomial in reduced density:

$$\log_{10}(1 + \Delta\eta*) = \sum_{i=1}^{7}a_i\left(\frac{1}{V*}\right)^i. \tag{5}$$

In order to address the second deficiency identified above, Ciotta [24] made use of experimental data for alkanes that extend into the high density region $V^* < 1.5$. For each substances and isotherm considered, the data at $V^* \ge 1.5$ were used to determine the reducing parameters R_η and V_0 that best map the experimental reduced viscosities on to the curve proposed by Assael et al. [7] The data at smaller reduced volumes were then used to establish the excess reduced viscosity as a function of reduced volume in an extended range spanning $1.25 \le V^* \le 1.5$. Ciotta [24] developed a correlation for $\Delta\eta^*(V^*)$ in the form of Eq. (5) by fitting these new data and by matching to the original scheme in the region $1.5 \le V^* \le 2.5$.