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# A kinetic theory description of the viscosity of dense fluids consisting of chain molecules

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An expression for the viscosity of a dense fluid is presented that includes the effect of molecular shape. The molecules of the fluid are approximated by chains of equal-sized, tangentially-jointed, rigid spheres. It is assumed that the collision dynamics in such a fluid can be approximated by instantaneous collisions between two rigid spheres belonging to different chains. The approach is thus analogous to that of Enskog for a fluid consisting of rigid spheres. The description is developed in terms of two molecular parameters, the diameter  $\sigma$  of the spherical segment and the chain length (number of segments)  $m$ . It is demonstrated that an analysis of viscosity data of a particular pure fluid alone cannot be used to obtain independently effective values of both  $\sigma$  and  $m$ . Nevertheless, the chain lengths of  $n$ -alkanes are determined by assuming that the diameter of each rigid sphere making up the chain can be represented by the diameter of a methane molecule. The effective chain lengths of  $n$ -alkanes are found to increase linearly with the number  $C$  of carbon atoms present. The dependence can be approximated by a simple relationship  $m = 1 + (C - 1)/3$ . The same relationship was reported within the context of a SAFT equation of state treatment of the fluid, indicating that both the equilibrium thermodynamic properties and viscosity yield the same value for the chain lengths of  $n$ -alkanes.

## I. INTRODUCTION

Molecular motion, and the resulting exchange of momentum and energy between colliding molecules, determine the thermophysical properties of a system. For dilute systems, where only the binary interactions are significant, both transport and thermodynamic properties can be related to the intermolecular forces by means of kinetic theory and statistical mechanics, respectively. For transport properties it has only recently become possible to perform these calculations essentially exactly for simple molecular fluids [1–3]. It has been shown that accurate transport properties are obtained and that viscosity, in particular, can be used to differentiate between a number of proposed *ab initio* intermolecular potentials.

For dense fluids the situation is less satisfactory. At present no rigorous theory exists for an exact evaluation of the thermophysical properties of a dense fluid in terms of realistic intermolecular potential-energy functions. A number of models have been proposed, the earliest and most famous being a rigid-sphere model. Despite its conceptual simplicity the rigid sphere model has been used as the basis of a number of predictive methods both for transport and thermodynamic properties [4, 5]. In order to achieve good accuracy most of the methods treat the size of the rigid sphere as an adjustable parameter,

that is, in some cases, allowed to be weakly temperature dependent as one would also expect from a classical perturbation theory of fluids [6]. In essence, the effective size implicitly allows for deficiencies of the rigid-sphere model. Not surprisingly, the analysis of transport properties yields different effective rigid sphere diameters to those obtained from an analysis of thermodynamic properties.

In recent years considerable effort has been made to extend the rigid sphere model to include the molecular shape and to allow for the treatment of both weak dispersive and strong associative (directional) attractive forces. These developments, culminating in statistical associating fluid theory (SAFT) [7–10], have been limited to thermodynamic properties; only limited empirical developments have been attempted for the transport properties, see for example [11, 12]. There are a number of reasons for this which centre upon the fact that, as the density increases, the effects of molecular velocity correlations and the effects of finite molecular volume become important. Although the formal Boltzmann integro-differential equation can be formulated, its general solution is not yet possible. Presently, the only tractable solution is based on Enskog’s rigid sphere analysis [13]. Although Enskog’s equations have been successfully adapted to predict the viscosity of both pure fluids [4] and mixtures [4, 14], success in predicting liquid mixture viscosity, for instance, has been limited to mixtures of similar-sized components [14]. For highly asymmetric mixtures, such as methane-decane, it has proved impossible to predict accurately the viscosity when assuming that both molecules can be represented as rigid spheres. Furthermore, the analysis

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of the viscosity of long chain molecules yields unphysical values for the effective size. This is not surprising considering that a fluid consisting of long chain molecules will shear differently to a fluid made of spheres. Hence, the inclusion of molecular shape becomes the first step in obtaining more physically-plausible viscosity models.

In this work, we extend Enskog's analysis by introducing molecular shape in expressions for the viscosity. In order to do this we model the molecules as tangentially-bonded chains of equal-sized rigid spheres. This choice of molecular model is driven by a number of factors. First, molecular dynamics simulation indicates that chain molecules elongate and align under shear [15]. Secondly, chain models have proved to be very successful in correlating the thermodynamic properties of many fluids and fluid mixtures, as demonstrated by the success of the SAFT approach [9, 10, 16, 17]. Finally, a hard chain model retains the essential simplicity of instantaneous point contact necessary to permit the Enskog-type solution. We further compare the effective chain parameters obtained by analysing the viscosity data to those employed in SAFT models.

It is important to note that the original approach of Wertheim [8, 18–21], which lies at the core of the SAFT equations of state, was formulated for chains of tangent spherical segments (so that the number of segments  $m$  is strictly an integer variable). One can however employ the ideas of scaled particle theory (SPT) to represent molecules formed from fused spherical segments in terms of models with non-integer values of the chain length  $m$  by using a direct analogy with the SPT non-sphericity shape factor [22–27]. A similar link between an effective chain length and related shape factors has also been made in more recent work [28, 29]. We make use of an effective chain length for models of chain molecules in the current paper.

## II. KINETIC THEORY

### A. Rigid spheres

The shear viscosity,  $\eta$ , of a pure fluid consisting of rigid spheres of diameter  $\sigma$  is given by Enskog's expression [13],

$$\eta = \eta^{(0)} \left( \frac{1}{\chi} + \alpha\rho + \frac{1}{\beta}\alpha^2\rho^2\chi \right), \quad (1)$$

where  $\rho$  is the molar density,  $\eta^{(0)}$  is the viscosity in the limit of zero density and constant  $\beta$  is equal to 0.8299. The function  $\chi$ , which depends on density, is the value of the radial distribution function at contact, while parameter  $\alpha$  is related to the excluded volume per molecule,  $V_{\text{excl.}}$ , through

$$\alpha = \frac{8N_A}{15}\pi\sigma^3 = \frac{2}{5}N_A V_{\text{excl.}}, \quad (2)$$

where  $N_A$  is Avogadro's constant.

There are a number of ways of expressing the radial distribution function at contact,  $\chi$ , in terms of the fluid density and the rigid sphere diameter  $\sigma$ . For example, either Lebowitz's solution of the Percus-Yevick equation [5, 30] or the Carnahan-Starling expression [31] may be used. Therefore, a knowledge of the rigid sphere diameter, together with the viscosity in the limit of zero density, should be sufficient to evaluate the viscosity of a pure fluid at any density. If the rigid sphere diameter is estimated in a standard way, from equilibrium thermodynamics, then the calculated viscosity will generally be much lower than that observed experimentally [4]. The failure of the Enskog rigid-sphere theory, in this instance, can be attributed, primarily, to the neglect of correlated motion. It is important to stress that the usefulness of Enskog's theory lies not in its ability to make predictions of the viscosity of dense fluids *a priori*, as the rigid-sphere assumption precludes that; rather it is important because it suggests a form of the viscosity-density relation that can be adapted to represent the behaviour of real fluids and their mixtures. Hence in the application of Eq. (1) to real fluids one needs to use an effective diameter. In practice this diameter tends to be weakly temperature dependent to account for the over simplification of the intermolecular forces implicit in the Enskog model. There are number of ways of estimating the effective diameter; here we focus on the solution successfully used as part of the VW method [14, 32, 33] for the prediction of the viscosity of fluid mixtures. The radial distribution function that will reproduce the observed fluid viscosity can be obtained by inverting Eq. (1) to give,

$$\chi(\rho, T) = \frac{\beta}{2\alpha^2\rho^2\eta^{(0)}} \left[ \eta - \alpha\rho\eta^{(0)} \pm \left( (\eta - \alpha\rho\eta^{(0)})^2 - \frac{4}{\beta}(\alpha\rho\eta^{(0)})^2 \right)^{\frac{1}{2}} \right]. \quad (3)$$

In general, the solution of Eq. (3) yields two roots,  $\chi^{(+)}$  and  $\chi^{(-)}$ , corresponding to the positive and negative

signs, respectively, of the bracketed quantity. To ensure a realistic physical behaviour, it is necessary to switch

from the  $\chi^{(-)}$  branch to the  $\chi^{(+)}$  branch of the solution at some particular molar density,  $\rho^*$ , at which the two roots become equal. This “switch-over density” is obtained from the solution of the equation [14, 33],

$$\left. \frac{\partial \eta}{\partial \rho} \right|_T = \frac{\eta}{\rho}. \quad (4)$$

If the switch-over density is chosen in this way, then the parameter  $\alpha$  can be determined uniquely, for a given isotherm [14, 33],

$$\frac{\eta^*}{\alpha \rho^* \eta^{(0)}} = 1 + \frac{2}{\sqrt{\beta}}, \quad (5)$$

where  $\eta^*$  is the value of the viscosity at the switch-over density. Hence, one can obtain, by means of Eq. (2) the effective diameter  $\sigma$  purely from the knowledge of the density dependence of viscosity, along a particular isotherm.

### B. Chains of rigid spheres

One of the underlying assumptions of Enskog’s rigid-sphere analysis is that interactions involving more than two particles almost never occur, and can therefore be neglected. In representing molecules as chains of equally sized rigid spheres we maintain that interactions between more than two chains are also negligible, and that three-particle interactions involving two spheres from the same chain are also rare. It is possible to envisage particular configurations of two chains in which this is not the case. For instance, a leading sphere of one of the chains can impact the other chain near the point where two spheres join and collide with both at nearly the same moment. In the present analysis we assume that these types of collisions can be neglected. Hence we assume that the collisions between two chains can be represented as collisions between two spheres belonging to different chains.

If we make these assumptions, we can extend Enskog’s analysis to chains. Equation (1) still holds but the radial distribution function refers to spherical segments making up the chains, and the parameter  $\alpha$  now refers to the excluded volume of a segment in the presence of another segment, given that both are bound up in chains. Not only the space occupied by a segment, but also that occupied by the chain attached to it is unavailable to the other segment or chain. As the two chains may not overlap the excluded volume of two segments bound in chains is the same as the excluded volume of two chains. Equation (1) becomes

$$\eta = \eta^{(0)} \left( \frac{1}{\chi} + \tilde{\alpha} \rho + \frac{1}{\beta} \tilde{\alpha}^2 \rho^2 \chi \right). \quad (6)$$

In this notation tilde above the symbol indicates a quantity with respect to chains and is used only to distinguish physical quantities where a confusion might arise. In the

limit of zero density, the radial distribution function of two chain segments at contact tends to  $\chi^{(0)}$ , not necessarily unity; while the viscosity tends to viscosity of molecules (chains) in the zero-density limit  $\tilde{\eta}^{(0)}$ . Taking the zero-density limit of Eq. (6), one obtains that

$$\tilde{\eta}^{(0)} = \frac{\eta^{(0)}}{\chi^{(0)}}, \quad (7)$$

where  $\eta^{(0)}$  is the zero-density limit of the viscosity of a fluid consisting of free spheres. If we assume that a chain is made up of  $m$  equal sized rigid spheres then we can define an average chain contact function  $\tilde{\chi}$  in terms of the compression factor  $Z$  as [34]

$$Z = 1 + 2\rho \tilde{\chi} \pi \sigma^3 / 3 = 1 + 4y \tilde{\chi}, \quad (8)$$

where  $y$  is the molecular packing fraction. Within the Wertheim first-order thermodynamic perturbation theory (TPT1) [20, 21] the compressibility factor of chains of hard spheres can be expressed in terms of the molecular packing fraction  $y$  as [8]

$$Z = 1 + m \frac{4y - 2y^2}{(1 - y)^3} - (m - 1) \frac{\frac{5}{2}y - y^2}{(1 - \frac{1}{2}y)(1 - y)}. \quad (9)$$

If one defines the contact value of the distribution function per spherical segment on the chain as

$$\chi = \frac{\tilde{\chi}}{m}, \quad (10)$$

then the average contact value of the distribution function between the chain segments can be expressed as

$$\chi = \frac{1 - \frac{1}{2}y}{(1 - y)^3} - \frac{m - 1}{m} \frac{\frac{5}{8} - \frac{1}{4}y}{(1 - \frac{1}{2}y)(1 - y)}. \quad (11)$$

In the zero density limit we have

$$\lim_{\rho \rightarrow 0} \chi = \chi^{(0)} = 1 - \frac{5(m - 1)}{8m}. \quad (12)$$

This means that for chains,  $m > 1$ , the contact value at zero density  $\chi^{(0)} < 1$ , which is consistent with correlation hole effects [35].

By replacing the molar density of free spheres  $\rho$  by the molar density of chains  $\tilde{\rho}$ , with

$$\rho = \tilde{\rho} m, \quad (13)$$

one can rewrite Eq. (6) and invert it to obtain an expression for  $\chi$  which is analogous to Eq. (3) for free rigid spheres. The solution will be constrained by

$$\frac{\eta^*}{\tilde{\eta}^{(0)} \chi^{(0)} \tilde{\alpha} m \tilde{\rho}^*} \equiv \frac{\eta^*}{\tilde{\eta}^{(0)} S \tilde{\rho}^*} = 1 + \frac{2}{\sqrt{\beta}}. \quad (14)$$

Hence, in analogy to the free-rigid-sphere case, one can obtain a parameter  $S$  from the density dependence of the

viscosity along a particular isotherm. In order to relate the parameter  $S$  to the geometry and size of the molecules we need to express the excluded volume parameter  $\tilde{a}$  in terms of the chain length  $m$  and diameter  $\sigma$ .

### III. EXCLUDED VOLUME

The parameter  $\tilde{a}$  is related to the excluded volume of two chains at contact by Eq. (2) with the proviso that all the quantities now refer to chains rather than spheres. Although for rigid spheres the relationship between the excluded volume and the volume of a single sphere is simply ( $V_{\text{excl.}} = 8V_{\text{sphere}}$ ), for non-spherical bodies, the relationship between the two volumes is not straightforward; primarily because the excluded volume depends on the geometry of the collision. For purposes of illustration we first present the expressions for the excluded volume of hard spherocylinders and then those of stiff linear chains consisting of tangent rigid spheres of equal size.

The expressions for the excluded volume in terms of the diameter  $\sigma$  and chain length  $m$  can then be used, together with Eqs. (2) and (12), to relate  $S$  and therefore the viscosity to the geometry and size of the molecules,

$$S = N_A \langle V_{\text{excl.}}(m, \sigma, \phi) \rangle \frac{(3m+5)}{20} = \frac{\eta^*}{\tilde{\rho}^* \tilde{\eta}^{(0)} (1 + \frac{2}{\sqrt{\beta}})} \quad (15)$$

where the  $\langle \dots \rangle$  indicates averaging over relative orientations and configurations at the time of collision. Substitution of these relations into equation (14) yields a relationship between the chain parameters and the viscosity at the switch-over density. Hence, it allows for the determination of either  $\sigma$  or  $m$  from the density dependence of viscosity, providing that the other parameter has been estimated by some other means.

#### A. Spherocylinders

One can approximate a stiff linear chain consisting of  $m$  rigid spheres of equal diameter  $\sigma$  by a rigid spherocylinder of the same diameter  $\sigma$  and total length  $m\sigma$ . The volume unavailable to such a spherocylinder in the presence of another spherocylinder is a function of the angle  $\phi$  between the axes of the two spherocylinders. It has a diamond shape with rounded ends, as illustrated in Fig 1.

The excluded volume can be separated into three parts, depending on the kind of contact, namely hemisphere-hemisphere, hemisphere-cylinder, and cylinder-cylinder. These result in corner, side and central core contributions, respectively, as depicted in Fig. 1. The total excluded volume can be written as a sum of these parts,

$$V_{\text{excl.}}^{\text{cyl.}}(m, \sigma, \phi) = V_{\text{cyl.}}^{(0)}(\sigma) + 2(m-1)V_{\text{cyl.}}^{(1)}(\sigma) + (m-1)^2 V_{\text{cyl.}}^{(2)}(\sigma, \phi), \quad (16)$$

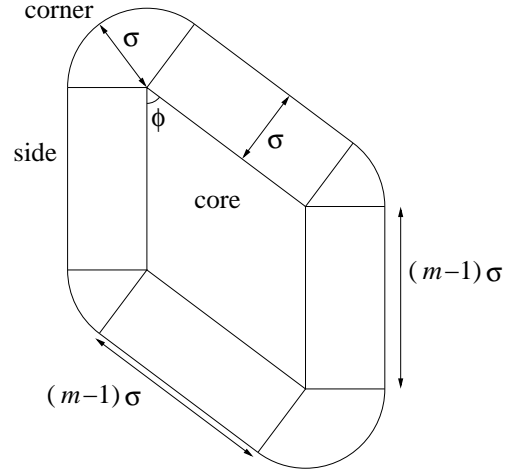


FIG. 1: The excluded volume of two spherocylinders, seen from the direction orthogonal to the axes of both spherocylinders.

where  $V^{(0)}$  denotes the total volume of corners,  $V^{(1)}$  the volume of a body section of length  $(m-1)\sigma$ , and  $V^{(2)}$  the volume of one unit cell of the central core. The central core is spanned by the unit vectors along each axis multiplied by the diameters, and a vector of length  $\sigma$  orthogonal to the plane of the diamond. Assuming that the orientations of the two spherocylinders are independent of each other, the total excluded volume for each contribution is obtained by integrating over all possible relative orientations,

$$\langle V \rangle = \int_0^{\pi/2} d\phi V(\phi) \sin \phi. \quad (17)$$

The corner contribution, due to contact between two hemispheres which is independent of  $\phi$ , is equal to

$$V_{\text{cyl.}}^{(0)}(\sigma) = \frac{4\pi}{3} \sigma^3 \quad (18)$$

The side contribution, due to interactions between a hemisphere and a cylinder, is also independent of the relative orientation,

$$V_{\text{cyl.}}^{(1)}(\sigma) = \pi \sigma^3. \quad (19)$$

Finally, the central core contribution for a given angle  $\phi$  is given by,

$$V_{\text{cyl.}}^{(2)}(\sigma, \phi) = 2\sigma^3 \sin \phi. \quad (20)$$

Combining equations (18)–(20) yields an excluded volume for two spherocylinders in terms of excluded volume of two spheres,

$$\langle V_{\text{excl.}}^{\text{cyl.}}(m, \sigma, \phi) \rangle = 8V_{\text{sphere}} \left( 1 + \frac{3}{2}(m-1) + \frac{3}{8}(m-1)^2 \right) \quad (21)$$

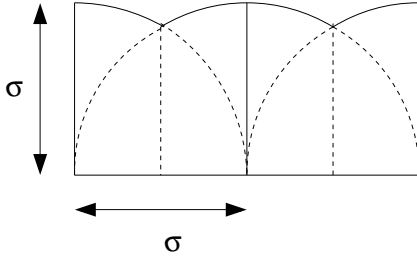


FIG. 2: Two unit cells of the side portion of the excluded volume of two stiff chains of spheres, seen from the direction orthogonal to the axes of both chains.

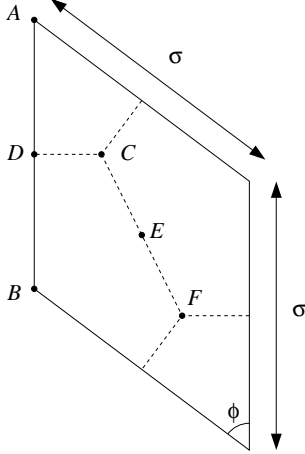


FIG. 3: A unit cell of the central core portion of the excluded volume of two stiff chains of spheres, seen from the direction orthogonal to the axes of both chain. A sphere of radius  $\sigma$  sits with its centre at each corner. The dotted lines indicate where the surfaces of the spheres meet. Point  $E$  is halfway between  $C$  and  $F$ .

This is the well-known results of Onsager [36] for the excluded volume of hard spherocylinders where the length of the cylindrical core is simply  $L = (m - 1)\sigma$ .

### B. Linear chains of rigid spheres

The same method that was used above to obtain the expression for the excluded volume of spherocylinders

can be used for stiff, linear chains consisting of  $m$  rigid spheres of diameter  $\sigma$ . The corner contribution is the same and is given by Eq. (18). The sides are no longer shaped like cylinders, but rather like slices of hemispheres with radii equal to  $\sigma$ , and centres that are a distance  $\sigma$  apart, see Fig. 2.

Taking both sides into account, the total side contribution is

$$V_{\text{chain}}^{(1)}(\sigma) = 4\sigma^3 \int_0^{\frac{1}{2}} dx \frac{\pi}{2} (1 - x^2) = \frac{11\pi}{12} \sigma^3. \quad (22)$$

A unit cell of the central core contribution is shown in Fig. 3. The volume of the central unit cell can be divided into segments of two different types, eight segments shaped like the volume indicated by triangle  $ACD$ , and four segments shaped like the volume indicated by  $BCE$  (cf. Figure 6 of reference [37]). Both types of segments have the same general shape with two parameters, the angle of the segment, denoted by  $\beta$ , which is equal to  $\angle CAD = \phi/2$  or  $\angle EBC = \pi/2 - \phi$  respectively, and the height compared to the radius, denoted by  $b$ , which is equal  $DA/\sigma = 1/2$  or  $EB/\sigma = \sin(\phi/2)$  respectively. The volume of such a segment of a unit sphere can be calculated from a double integral,

$$V_{\Delta}(\beta, b) = \int_0^b dx \int_0^{x \tan \beta} dy 2\sqrt{1 - x^2 - y^2}. \quad (23)$$

The volume of a unit cell is found by summing over all the segments,

$$V_{\text{chain}}^{(2)}(\sigma, \phi) = \sigma^3 \left[ 8V_{\Delta}\left(\frac{\phi}{2}, \frac{1}{2}\right) + 4V_{\Delta}\left(\frac{\pi}{2} - \phi, \sin\frac{\phi}{2}\right) \right] \quad (24)$$

Finally, the averaging over the relative orientation, followed by tedious integration, yields

$$\langle V_{\text{chain}}^{(2)}(\sigma, \phi) \rangle = \frac{1}{10} \left( 11\pi - 18 \arctan \sqrt{2} - 2\sqrt{2} \right) \sigma^3 \quad (25)$$

$$\approx 1.45334 \sigma^3. \quad (26)$$

The final result for the excluded volume for a linear chain of  $m$  tangent segments can be expressed in a new compact form as

$$\langle V_{\text{excl.}}^{\text{chain}}(m, \sigma, \phi) \rangle = 8V_{\text{sphere}} \left[ 1 + \frac{11}{8}(m - 1) + \frac{3}{40\pi} \left( 11\pi - 18 \arctan \sqrt{2} - 2\sqrt{2} \right) (m - 1)^2 \right]. \quad (27)$$

An essentially equivalent result is obtained in Ref. [37] by a different more involved route making use of the exact expression for the second virial coefficient determined by Isihara [38]; Isihara presents the correspond-

ing integrals for the general case of fused hard diatomics (the tangent dimer  $m = 2$  being a special case) in a complicated irrational form. The second virial coefficient of a tangent dimer obtained from equation (27) is

$B_2^* = B_2/(mV_{\text{sphere}}) = \langle V_{\text{excl.}} \rangle / (2mV_{\text{sphere}}) = 5.44392$  which is the same as the Isihara result. Comparing Eqs. (21) and (27), we see that the coefficients of  $(m-1)$  and  $(m-1)^2$  in the expression for the excluded volume of a stiff chain are both approximately 8% smaller than those for the spherocylinder. The two excluded volume expressions therefore differ by 8% for large  $m$ .

Strictly one should be considering fully flexible chains as this is the model used in deriving the TPT1 thermodynamics of chains and is a more realistic representation of real molecules. If the chains are not stiff, but floppy, the shape of the excluded volume becomes much more complicated. Fynnever and Yethiraj [39] have examined the excluded volumes of flexible chains of this type at fixed relative orientations and have fitted their fully numerical results (obtained with a continuum configurational bias Monte Carlo method) to a simpler algebraic form. Though one could use these empirical forms for the excluded volume of flexible chains we opt for the more rigorous results of the linear models as in any case the thermodynamic properties of the two systems are the same at the Wertheim TPT1 first-order level. When the chains curl back on themselves, it is possible for the excluded volume to intersect with itself. As long as these intersections do not represent much volume, the total excluded volume of the floppy chains can be approximated reasonably well by the excluded volume of stiff chains. This is the case when the typical radius of the curvature of the floppy chains is large compared to the diameter of the segments.

### C. Viscosity

Using the spherocylinder or stiff-chain results for the excluded volume  $V_{\text{excl.}}$ , equations (21) and (27) respectively, and Eq. (15) one can express the parameter  $S$  in terms of the chain length and diameter of a molecule. Hence, one can determine either  $\sigma$  or  $m$  from the density dependence of the viscosity, providing that the other parameter has been estimated by some other means. We outline such a procedure in the following section.

## IV. ALKANES

### A. Methane

In order to examine the adequacy of the chain concept in describing the viscosity of real fluids we start by applying the developed model to alkanes. The first member of the alkane family, methane, interacts through an intermolecular potential [40] that is sufficiently spherical that we can represent the molecule by a single rigid sphere. Hence we can use Eq. (5) to determine the parameter  $\alpha$ , and subsequently the diameter  $\sigma$ , from the analysis of the viscosity behaviour as a function of density for a given isotherm. The viscosity of pure methane was obtained

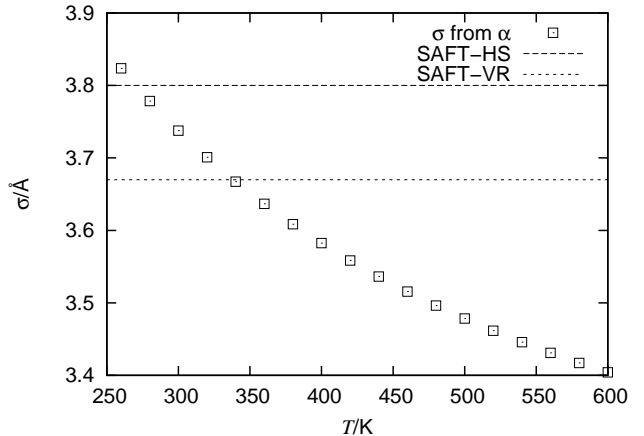


FIG. 4: The diameter of methane calculated from  $\alpha$  obtained from the density dependence of the viscosity [41], along with SAFT-HS results from [17] and SAFT-VR results from [16].

from the representation of Vogel *et al.* [41]. The correlation covers a temperature range from 100 K to 600 K and a pressure range up to 100 MPa. The estimated uncertainty is of the order of 1-3%, in the temperature and density range of interest to this work. In Figure 4 we illustrate the behaviour of the effective rigid sphere diameter  $\sigma$  as a function of temperature. A small temperature variation, of the order of 10%, is observed, the effective diameter decreasing with increasing temperature. The decrease in the diameter indicates, as expected, that for real fluids the repulsive part of the intermolecular potential is steep but not infinitely steep as in the rigid sphere model. The effective diameter obtained from the thermodynamic SAFT-HS [17] and SAFT-VR [16] models are also denoted on Figure 4. For the hard-core (hard-sphere and square-well) models employed with SAFT-HS and SAFT-VR, the effective diameter does not vary with temperature and its value is within the range of values obtained by analysing the viscosity data. The general agreement between the SAFT-HS, SAFT-VR and viscosity values of the effective diameter  $\sigma$  indicates that the deficiencies of Enskog's theory in describing the viscosity are primarily taken up by the effective radial distribution function, equation (3); while the deficiencies of the rigid sphere model in describing the intermolecular forces manifest themselves in the temperature dependence of the effective diameter,  $\sigma$ .

### B. Higher alkanes

We represent the rest of the  $n$ -alkanes as chains of  $m$  rigid spheres of equal size. We assume, in line with the transferable parameter treatment undertaken with SAFT-HS [17], that the diameter of each spherical segment is given by the diameter of a methane molecule at that temperature. Hence, we maintain the distinction that all the parameters in the analysis are obtained from

knowledge of viscosity, rather than fluid-phase equilibrium properties. From an analysis of viscosity of alkanes we determine the parameter  $S$  by means of Eq (14) for a given temperature. As the effective diameter  $\sigma$  is known, at each temperature, we can determine the effective chain length  $m$  for each alkane.

## V. RESULTS

For an accurate calculation of  $m$  it is essential to make use of viscosity data for the pure components that are accurate and reliable. For this purpose we choose the currently recommended viscosity correlations that are based on critical assessments of the available experimental data with well-defined accuracy. The viscosity of ethane was taken from the correlation of Hendl *et al.* [42] and had an uncertainty of up to 3%. The correlation extends over the temperature range from 200 K to 1000 K for pressures up to 60 MPa. The viscosities of propane and  $n$ -butane, were described with the correlations of Vogel and co-workers [43, 44] who reported uncertainties ranging from 3 to 6% in the range of interest to this work. The temperature and pressure range of propane and  $n$ -butane correlations extended to 600 K, 100 MPa and 500 K, 70 MPa, respectively. For the higher alkanes there are no available correlations that are based on a critical assessment of the experimental data. To generate the viscosity for these fluids we made use of the Assael and Dymond correlation [45] that is formulated in terms of the corresponding states principle. The accuracy of the correlation, based on comparison with the available experimental data, is of the order of 5-8%. The viscosity in the limit of zero density,  $\eta^{(0)}$ , for lower alkanes was obtained directly from the available correlations [41–44]. For  $n$ -pentane and higher alkanes the zero-density viscosity was obtained either from an analysis of the available experimental gas viscosity data or from the general corresponding states correlation of Lucas and co-workers [46].

In Figure 5 we illustrate the behaviour of  $m$  as a function of temperature for a selected set of linear alkanes, in the temperature range where the viscosity correlations are valid. The calculations of the chain lengths were performed both for spherocylinders, Eq. (21), and linear chains of spherical segments, Eq. (27). The difference in the chain lengths obtained from the two models is small. One remarkable feature apparent from Fig. 5 is that the chain lengths are nearly independent of temperature when the uncertainty of the viscosity data, used in their estimation, is taken into account. This indicates that the temperature dependence of the effective diameter is similar for all the alkanes and can be represented by that of methane. The universality of this function further indicates that the steepness of the effective spherical repulsive part of the intermolecular potential function for alkanes is similar. This corroborates the success of a number of predictive schemes that are based on universal correlations [4, 45].

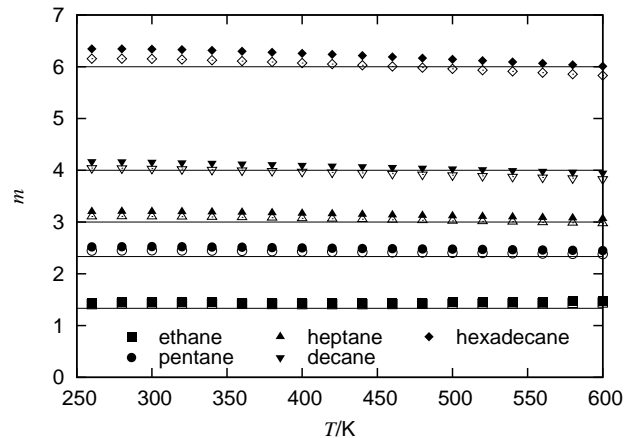


FIG. 5: Chain lengths of selected  $n$ -alkanes, estimated from viscosity, as a function of temperature. The open symbols represent the corresponding values for spherocylinders.

The corresponding variation of effective chain length,  $m$ , with the number of carbon atoms  $C$  is shown in Figure 6. The relationship is linear and can be approximated by  $m = 1 + (C - 1)/3$ . The approximation can be rationalised by the fact that the carbon-carbon bond length in  $n$ -alkanes is roughly a third of the diameter of a methane molecule. What is remarkable is that the same relationship with a fixed size rigid spheres, used in SAFT-HS, successfully correlates the critical properties of alkanes [17]. A good description was obtained for the critical volumes and critical pressure and temperature, although the critical pressure of methane was overestimated and the critical temperature of methane and ethane were underestimated. Furthermore, a free fit of  $m$  to the experimental vapour pressures and saturated liquid densities of alkanes for a square-well model within SAFT-VR [16] leads to an equivalent relationship between  $m$  and  $C$ .

The viscosity data of the pure fluids cannot be used to obtain independently the values of both  $\sigma$  and  $m$ , instead it yields a value for the single effective size parameter  $S$ . In principle one is free to choose any combination of  $\sigma$  and  $m$  that satisfy Eq. (15). One could stipulate that  $m$  should be restricted to integer values only, to maintain its physical meaning. However, the non-integer value of  $m$  can be viewed as a measure of the aspect ratio (or shape) of a molecule, rather than a number of rigid spheres. Nevertheless, the final choice of  $m$  and  $\sigma$  will have to be based on the ability of the proposed chain model to predict the viscosity of mixtures, especially of mixtures consisting of molecules of dissimilar size.

In principle, there is no need to restrict the approach described in this paper to  $n$ -alkanes. The main results hold also for non-linear isomers. However, expressions for the excluded volume of branched objects are much more complicated than those of simpler linear objects. In SAFT-VR sometimes branched molecules are treated as effectively unbranched with reasonable success.



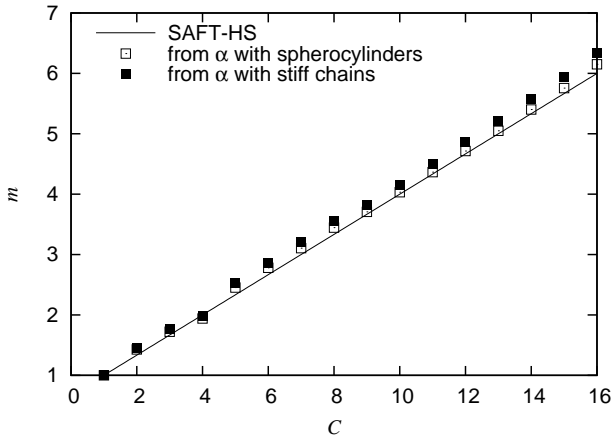


FIG. 6: Chain lengths of  $n$ -alkanes estimated from viscosity as a function of the number of carbon atoms, at 300 K. For propane and butane a temperature of 500 K was used. The analysis of the viscosity along the 300 K isotherm, for propane and butane, indicates that the switch-over density occurs deep in the two-phase region, which introduces an additional uncertainty in the determination of  $m$ . A single-parameter fit with the function  $a(C - 1) + 1$  gives  $a = 0.354 \pm 0.004$  for stiff chains of spheres, and  $a = 0.340 \pm 0.003$  for spherocylinders

## VI. CONCLUSION

Enskog's expression for the viscosity of a dense fluid made up of rigid spheres has been extended to hard-chain fluids. We assume that the collision dynamics of chains of rigid spheres can be approximated by the instant collision of two rigid spheres belonging to different chains. For realistic high-density fluids, the resulting description suffers from the same deficiencies as Enskog's theory. In particular, it cannot be used *a priori* to predict the viscosity from the knowledge of the size and shape of the molecules; the neglect of correlated motion precludes such an approach.

Nevertheless, it has been shown that the derived viscosity expression can be used, in a manner proposed by the VW methodology [14, 33], to obtain a single, temperature-dependent effective size parameter from an analysis of the viscosity as a function of density for a given isotherm. The size parameter is further related to two molecular parameters that describe the size and shape of the molecules, namely the diameter of the rigid spheres,  $\sigma$ , making up the chain and the chain length,  $m$ , through analytical expressions for the excluded volume of two linear chains and for the purpose of comparison the equivalent expression for spherocylinders. The proposed model therefore relates the viscosity of a pure fluid to two molecular parameters  $\sigma$  and  $m$ .

The derived expressions are used to obtain the effective diameter of the methane molecule under the assumption that it can be represented by a single rigid sphere. The effective diameter was shown to be weakly temperature dependent indicating a finite steepness (softness) of the real repulsive part of the intermolecular potential.

The expressions are then applied to the analysis of the best available viscosity data for  $n$ -alkanes. For this purpose, the  $n$ -alkanes were modelled as chains of length  $m$  consisting of rigid spheres of diameter equal to that of methane, at a given temperature. From this analysis we find that the effective chain lengths are nearly independent of temperature. This indicates that the temperature dependence of the effective diameter for all alkanes can be represented by that of methane.

The analysis further suggests that the effective chain lengths of  $n$ -alkanes increase linearly with the number of carbon atoms present. The dependence can be approximated by a simple relationship  $m = 1 + (C - 1)/3$ . The same relationship was obtained from the SAFT analysis of thermodynamic properties [16, 17]. It is interesting that both the thermodynamic and transport properties yield equivalent values for the lengths of the  $n$ -alkanes.

One would not expect that the use of the excluded volume of a linear chain in the description of the viscosity of real flexible chain molecules to cause a particular problem. It has been shown that the though flexibility is important in determining the stability or otherwise of anisotropic phases such as the nematic, the thermodynamic properties of the isotropic phase of flexible or of linear hard-sphere chains turn out to be very similar (compare the findings of [39] with [47]).

The primary application of these new findings will be in relation to the VW methodology for the prediction of viscosity of mixtures of non-spherical molecules. In particular, we expect the hard-chain approach to permit a reliable predictions to be made for highly asymmetric mixtures where the current hard-sphere VW approach fails entirely. We have shown that the analysis of the viscosity data of the pure fluids cannot be used to independently obtain the values of  $\sigma$  and  $m$ . Nevertheless, the near equivalence of chain length,  $m$ , obtained from the viscosity and SAFT indicates that in principle the SAFT values can be adopted and the effective parameter  $\sigma$  determined uniquely from the analysis of viscosity. The final choice of  $m$  and  $\sigma$  will have to be based on the ability of the proposed chain model to predict the viscosity of mixtures, especially of mixtures consisting of molecules of dissimilar size. This is a the topic of on-going research.

In principle, another reference compound can be used to determine  $\sigma$ , as long as the monomers are similar, and the chain length is known. This method only works if there is a suitable reference compound with a well-known chain length. When considering compounds with bonds that are not single bonds between carbon or hydrogen atoms, one could obtain information about bond lengths from different compounds. For instance, when one is interested in the shape of molecules of OH bonds, one could use the density-dependence of the viscosity of ethanol to obtain information about the size of such bonds, and information about carbon double bonds could be obtained from ethylene.

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