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Viscosity of liquid mixtures: The Vesovic-Wakeham method for chain molecules

Astrid S. de Wijn,[1,2] Nicolas Riesco,[2,3] George Jackson,[4] J. P. Martin Trusler,[4]
and Velisa Vesovic[2,a)]
[1]*Institute for Molecules and Materials, Radboud University Nijmegen, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands*
[2]*Department of Earth Science and Engineering, South Kensington Campus, Imperial College London, London SW7 2AZ, United Kingdom*
[3]*Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), Department of Earth Science and Engineering, South Kensington Campus, Imperial College London, London SW7 2AZ, United Kingdom*
[4]*Department of Chemical Engineering, South Kensington Campus, Imperial College London, London SW7 2AZ, United Kingdom*

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New expressions for the viscosity of liquid mixtures, consisting of chain-like molecules, are derived by means of Enskog-type analysis. The molecules of the fluid are modelled as chains of equally sized, tangentially joined, and rigid spheres. It is assumed that the collision dynamics in such a fluid can be approximated by instantaneous collisions. We determine the molecular size parameters from the viscosity of each pure species and show how the different effective parameters can be evaluated by extending the Vesovic-Wakeham (VW) method. We propose and implement a number of thermodynamically consistent mixing rules, taking advantage of SAFT-type analysis, in order to develop the VW method for chain molecules. The predictions of the VW-chain model have been compared in the first instance with experimental viscosity data for octane-dodecane and methane-decane mixtures, thus, illustrating that the resulting VW–chain model is capable of accurately representing the viscosity of real liquid mixtures. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3685605]

I. INTRODUCTION

Understanding the relationship between the macroscopic transport properties of fluids and the interactions among individual molecules is the ultimate goal of kinetic theory. The last decade has witnessed great advances in our ability to calculate the transport properties of fluids directly from intermolecular forces.[1–10] Such calculations do not only improve our insight into the dominant microscopic processes, but also allow us to develop more accurate and reliable methods for the prediction of transport properties. Although it is essential to validate such methods against a bank of high-quality experimental data, the reliance purely on experimental data and empirical correlations based on them is not sufficient, especially as there is an urgent need to facilitate a reliable prediction of the viscosity of liquid mixtures over wide ranges of temperature, pressure and composition.

At present, there is no rigorous kinetic theory that allows for the calculation of the viscosity of a dense fluid from a realistic intermolecular potential. The lack of a general solution of the formal Boltzmann integro-differential equation is still a fundamental unresolved problem. So far the only tractable solutions have been based on simplifying the intermolecular interaction by assuming that molecules in the fluid interact as hard spheres and that molecular collisions are uncorrelated. For such a system it is possible, through Enskog's analysis,[11,12] to derive a relationship between the viscosity of the fluid and molecular parameters. The Enskog equation, though approximate in nature, has nevertheless provided a useful theoretical basis for both understanding and predicting the viscosity of fluids.[13,14] Notwithstanding the recent advances in molecular dynamics[3–6,10] and density-fluctuation theory[15,16] all indications are that it will remain a cornerstone for the development of viscosity models based on kinetic theory.

Recently, Enskog's analysis has been extended to incorporate molecular shape (size asymmetry) in the expressions for the self-diffusion coefficient[17–19] and the viscosity.[20] Molecules were modelled as chains formed from equally sized hard spheres. Chain models provide a very useful link, at the molecular level, with the Wertheim TPT1 (Refs. 21–23) and statistical associating fluid theory (SAFT) (Ref. 24 and 25) that has proved to be very successful in describing the thermodynamic properties of a wide variety of fluids and fluid mixtures. In principle, representing molecules as chains provides a further degree of realism and should allow for a more accurate description of the viscosity of the fluid. However, the resulting viscosity model is still based on Enskog-type collision dynamics and the postulates of instantaneous collisions and uncorrelated molecular motion.[12] It therefore suffers from the same deficiencies as the original hard-sphere (HS) model. This renders it unsuitable for *a priori* predictions of viscosity or any other transport properties. For the original hard-sphere model

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[a)] Author to whom correspondence should be addressed. Electronic mail: v.vesovic@imperial.ac.uk.

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this can be circumvented by using effective hard-sphere diameters that are weakly temperature dependent.[13,14] A proper choice of the effective diameter is paramount for success in representing the viscosity of the fluid. For fluid mixtures, the problem of choosing the appropriate effective diameters is compounded by the presence of more than one species. In order to address this problem, Vesovic and Wakeham (VW) (Ref. 26) proposed that the effective parameters for a mixture are obtained from the viscosity of pure species. This choice of effective parameters is at the heart of the development of the VW method[26,27] that can be used to predict accurately the viscosity of a variety of different mixtures, including natural gas,[28] refrigerant,[29] and supercritical fluid mixtures.[26,27] The accuracy can be retained when predicting the viscosity of liquid mixtures[27,29] providing the systems contain molecules of similar molecular mass and size, thus allowing for a representation of each molecule by an effective hard sphere. If the molecules are different in size the hard-sphere representation is no longer adequate and a chain representation becomes more appropriate, if the accuracy is to be retained.

In our current work we first present expressions for the viscosity of liquid mixtures consisting of chain-like molecules that are derived with an Enskog-type analysis. We then show how the different effective parameters can be evaluated by extending the VW method. Finally, we illustrate through two examples that the resulting VW–chain model is capable of accurately representing the viscosity of real liquid mixtures.

The development of the VW-chain model is primarily driven by the needs of the petroleum industry, where the knowledge of oil viscosity is essential for optimal exploitation of oil reservoirs. Reservoir fluids are complex mixtures consisting of a large number of hydrocarbons, predominantly chain molecules. In order to develop accurate and reliable predictions of viscosity of such mixtures it is essential to take a proper account of the shape of the molecules making up the mixture.

II. MODEL AND THEORY

In this section, we present an expression for the viscosity of a liquid mixture that consists of molecules represented as chains of hard spheres. The new expression is derived by combining the Enskog-like analysis for hard-spheres[11,12] and our recent work[20] on chain molecules.

A. The viscosity of a pure chain-fluid

A hard-sphere fluid consists of spheres of diameter σ that interact only on contact.[30,31] If we assume that the collisions between the hard spheres are uncorrelated (i.e., molecular chaos) then the shear viscosity, η, of such a fluid can be described with Enskog's expression:[12]

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

where ρ is the molar density, $\eta^{\,(0)}$ is the viscosity in the limit of zero density, and β is a constant equal to $(1/4 + 3/\pi)^{-1}$. The quantity χ is the radial distribution function at contact, while α is a parameter proportional to the excluded volume per molecule, V_{excl},

$$\alpha = \frac{8}{15}N_A\pi\sigma^3 = \frac{2}{5}N_A V_{excl}, \tag{2}$$

where N_{A} is Avogadro's constant.

Considerable effort has been made to extend the hard-sphere model to fluids of non-spherical molecules. One way of including the non-sphericity is to model the molecules as tangentially bonded chains consisting of equally-sized, hard, spherical segments. Such a representation of real fluids has been very successful for the description of thermodynamic properties and has recently been extended by ourselves[20] to treat the system's viscosity. With this type of approach, the viscosity of a fluid consisting of N chains, each made up of m segments, can be approximated in the dense region by that of a fluid consisting of mN hard-spheres. We refer to this fluid as a segment fluid. In such a fluid, the collision dynamics is governed principally by collisions between segments and one can make use of Enskog's approach. However, the collision rate is still affected by the neighbouring segments in the chain, and the resulting viscosity expression,

$$\eta = \tilde{\eta}^{(0)}\left[\frac{1}{\tilde{\chi}} + \tilde{\alpha}\tilde{\rho} + \frac{1}{\beta}\tilde{\alpha}^2\tilde{\rho}^2\tilde{\chi}\right], \tag{3}$$

now involves quantities defined on a per segment basis, indicated here by the tilde. Unlike in Ref. 20, in order to avoid confusion here between the usual symbol for viscosity in the zero-density limit, $\eta^{(0)}$, and the corresponding parameter in the segment fluid, $\tilde{\eta}^{(0)}$, a tilde is used to indicate a quantity defined for segments. The segment density $\tilde{\rho}$ is given by $\tilde{\rho} = \rho m$, while $\tilde{\alpha}$ is a parameter proportional to the excluded volume of a segment in the presence of another. As the segments in the same chain screen each other from collisions, the excluded volume of each segment still corresponds to the excluded volume of a chain.[20] Hence, the parameter $\tilde{\alpha}$ can be approximated as

$$\frac{\tilde{\alpha}}{\tilde{\alpha}_{segment}} = 1 + \frac{3}{2}(m-1) + \frac{3}{8}(m-1)^2, \tag{4}$$

where $\tilde{\alpha}_{segment}$ is the excluded volume of the free segment, $4\pi\sigma^3/3$.

The zero-density viscosity of the segments $\tilde{\eta}^{(0)}$ is related to the zero-density viscosity of the fluid by the expression,[20]

$$\tilde{\eta}^{(0)} = \eta^{(0)}\tilde{\chi}^{(0)} = \eta^{(0)}\left(1 - \frac{5}{8}\left(\frac{m-1}{m}\right)\right). \tag{5}$$

We refer the reader to Ref. 20 for the details of the derivation of Eqs. (4) and (5), but also point out that Eq. (4) is a well-known result by Onsager[32] for the excluded volume of hard spherocylinders, while Eq. (5) is consistent with the correlation hole effect.[33]

B. The viscosity of chain-fluid mixture

In the present paper, we extend the Enskog-Thorne approach[12,34] for evaluating the viscosity of mixtures of hard spheres to mixtures where the molecules are represented as

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chains made up of hard, spherical segments. We consider the molecules of component i as chains consisting of m_i segments with a mass given by $\tilde{M}_i = M_i/m_i$, where M_i is the molecular mass.

We are primarily interested in developing a model that allows for the prediction of the viscosity of liquid mixtures. Hence we constrain both the model and the discussion to liquid-like densities. In the dense fluid, the collision rate is high and in general the mean-free path between the collisions is smaller than the size of the segments. It is thus reasonable to assume that a particular segment will undergo a number of collisions before the effects of the initial collision are felt further down the chain. We therefore postulate that, at liquid-like densities, as far as the collision dynamics is concerned, a fluid consisting of chain molecules can be described as an analogous fluid consisting of unbound or weakly-bound segments. The viscosity of such a mixture consisting of chain molecules can then be obtained by following Enskog-Thorne approach and is given by:

$$\eta = \tilde{K}_{mix} - \frac{\begin{vmatrix} \tilde{H}_{11} & \dots & \tilde{H}_{1N} & \tilde{Y}_1 \\ \vdots & \ddots & \vdots & \vdots \\ \tilde{H}_{N1} & \dots & \tilde{H}_{NN} & \tilde{Y}_N \\ \tilde{Y}_1 & \dots & \tilde{Y}_N & 0 \end{vmatrix}}{\begin{vmatrix} \tilde{H}_{11} & \dots & \tilde{H}_{1N} \\ \vdots & \ddots & \vdots \\ \tilde{H}_{N1} & \dots & \tilde{H}_{NN} \end{vmatrix}}, \tag{6}$$

$$\tilde{K}_{mix} = \frac{3\tilde{\rho}^2}{\pi} \sum_{i,j} \tilde{x}_i \tilde{x}_j \tilde{\chi}_{ij} \tilde{\alpha}_{ij}^2 \tilde{\eta}_{ij}^{(0)}, \tag{7}$$

$$\tilde{Y}_i = \tilde{x}_i \left[1 + \tilde{\rho} \sum_j \frac{\tilde{M}_j}{\tilde{M}_i + \tilde{M}_j} \tilde{x}_j \tilde{\alpha}_{ij} \tilde{\chi}_{ij} \right], \tag{8}$$

$$\tilde{H}_{ij} = \frac{-\tilde{x}_i \tilde{x}_j \tilde{\chi}_{ij}}{2\mathrm{A}_{ij}^* \tilde{\eta}_{ij}^{(0)}} \frac{\tilde{M}_i \tilde{M}_j}{(\tilde{M}_i + \tilde{M}_j)^2} \left[\frac{20}{3} - 4A_{ij}^* \right], \tag{9}$$

$$\tilde{H}_{ii} = \tilde{x}_i^2 \frac{\tilde{\chi}_{ii}}{\tilde{\eta}_i^{(0)}} + \sum_{j \neq i} \frac{\tilde{x}_i \tilde{x}_j \tilde{\chi}_{ij}}{2\mathrm{A}_{ij}^* \tilde{\eta}_{ij}^{(0)}} \frac{\tilde{M}_i \tilde{M}_j}{(\tilde{M}_i + \tilde{M}_j)^2} \left[\frac{20}{3} + 4\frac{\tilde{M}_j}{\tilde{M}_i} A_{ij}^* \right], \tag{10}$$

where $\tilde{\rho} = (\sum_i x_i m_i)\rho$ is the segment density, x_i is the mole fraction of component i, and $\tilde{x}_i = x_i m_i / (\sum_j x_j m_j)$ is the segment fraction. The quantities $\tilde{\eta}_{ij}^{(0)}$ and A_{ij}^* are the segment interaction viscosity and ratio of collision integrals,[35,36] respectively, for the i-j pair in the limit of zero density. The parameter $\tilde{\alpha}_{ij}$ is the excluded volume of a segment of a chain of species i in the presence of a segment of a chain of species j while $\tilde{\chi}_{ij}$ represents the segment-segment radial distribution function at contact for the species i and j in the presence of all other species in the mixture. In Sec. II C we examine how to obtain the relevant pure species properties, in order to combine them using mixing rules discussed in the subsequent Sec. II D.

C. The VW method for chain molecules

In principle, knowledge of the excluded volume and the radial distribution function at contact, both of which can be obtained from thermodynamic considerations, together with the pure component viscosities in the limit of zero density, would be sufficient to evaluate the viscosity of any pure fluid or fluid mixture. However, if Enskog's theory is used in its original form then generally the predicted viscosity will be much higher than that observed experimentally. There are number of ways of modifying the Enskog expressions in order to predict the behaviour of real fluids.[14] In our current work we focus on the solution successfully used as part of the VW method[26–29] and extend the VW method to mixtures modelled as chains formed from hard segments.

The crux of VW method is to obtain the effective radial distribution function at contact from the experimentally determined viscosity of each pure species, thus ensuring that, in the limit of each pure species, viscosity of the mixture tends to a correct value. This is achieved by inverting Eq. (3) in quadratic form

$$\tilde{\chi}_i^{\pm} = \frac{\beta}{2\tilde{\rho}_i \tilde{\alpha}_i} \left[\left(\frac{\eta}{\tilde{\rho}_i \tilde{\alpha}_i \tilde{\eta}_i^{(0)}} - 1 \right) \pm \sqrt{ \left(\frac{\eta}{\tilde{\rho}_i \tilde{\alpha}_i \tilde{\eta}_i^{(0)}} - 1 \right)^2 - \frac{4}{\beta} } \right]. \tag{11}$$

To ensure realistic physical behaviour, it is necessary to switch from the $\tilde{\chi}_i^-$ branch to the $\tilde{\chi}_i^+$ branch of the solution at some particular density, $\tilde{\rho}_i^* = m_i \rho_i^*$, at which the two roots are equal. This "switch-over density" can be obtained[37] from the solution of

$$\left(\frac{\partial \eta_i}{\partial \rho} \right) = \frac{\eta_i^*}{\rho_i^*}. \tag{12}$$

The use of Eq. (12) ensures a unique value of parameter $\tilde{\alpha}_i$, namely,

$$\tilde{\alpha}_i = \frac{\eta_i^*}{\tilde{\rho}_i^* \tilde{\eta}_i^{(0)} \left(1 + \frac{2}{\sqrt{\beta}}\right)}. \tag{13}$$

It is important to stress that although $\tilde{\alpha}_i$ and $\tilde{\chi}_i$ determined in this fashion are unique, they are effective parameters. In the process of using them to reproduce the viscosity of pure species, the link between the two, in terms of the hard-sphere diameter, has been broken. What this confirms is that Enskog's expression, Eq. (1), does not adequately describe the viscosity of a real fluid, even if we allow the hard-sphere diameter to become an effective parameter dependent on temperature. There is no reason to believe that a single effective diameter can correctly account for the simplifications to both the dynamics and the geometry of the molecular interactions that Enskog introduced. In essence the VW method postulates that in order to reproduce the experimental viscosity by means of a hard-sphere fluid one needs to use one effective size of the molecule for the excluded volume and another for the collisional dynamics.

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Hence, we differentiate between the two diameters, $\tilde{\sigma}_{\alpha,i}$ and $\tilde{\sigma}_{\chi,i}$, using the subscript α to indicate that it was obtained from the parameter α by means of Eq. (13) and the subscript χ to indicate that it has been obtained from the radial distribution function at contact, Eq. (11). These effective diameters are distinguished further by the subscript "*i*" to indicate that they can take a different value for different species.

In order to be able to use Eqs. (6)–(10) to calculate the viscosity of a mixture, we need to relate the properties of the pure species segments to those for the *i*-*j* binary interaction.

D. Estimating the mixture interaction parameters

1. Estimating the effective mutual excluded volume, $\tilde{\alpha}_{ij}$

It is important to stress that the mutual excluded volume of a segment of a chain of species *i* in the presence of a segment of a chain of species *j* is different to the excluded volume of two free segments. The excluded volume of two segments, belonging to two chains, is in fact equal to the excluded volume of the two chains. The chain excluded volume can be approximated by the mutual excluded volume of two spherocylinders of the same lengths as the chains,[20]

$$\frac{\tilde{\alpha}_{ij}}{\tilde{\alpha}_{segment,ij}} = 1 + \frac{3}{2}\left(\frac{\left(\frac{\tilde{\alpha}_{segment,i}}{\tilde{\alpha}_{segment,ij}}\right)^{1/3}(m_{\alpha,i}-1) + \left(\frac{\tilde{\alpha}_{segment,j}}{\tilde{\alpha}_{segment,ij}}\right)^{1/3}(m_{\alpha,j}-1)}{2}\right) + \frac{3}{8}\left(\frac{\tilde{\alpha}_{segment,i}}{\tilde{\alpha}_{segment,ij}}\right)^{1/3}(m_{\alpha,i}-1)\left(\frac{\tilde{\alpha}_{segment,j}}{\tilde{\alpha}_{segment,ij}}\right)^{1/3}(m_{\alpha,j}-1), \tag{14}$$

where $m_{\alpha,i}$ is the number of segments of chain of species *i*.

We obtain the expression for the unlike *i*-*j* interaction of segments by simply invoking the arithmetic result that the excluded volume of two spheres of unequal diameter is related to that with the average diameter (additive spheres),

$$\begin{aligned}\tilde{\alpha}_{segment,ij}^{1/3} &= \frac{1}{2}\left(\tilde{\alpha}_{segment,i}^{1/3} + \tilde{\alpha}_{segment,j}^{1/3}\right)\\ \propto \tilde{\sigma}_{\alpha,ij} &= \frac{1}{2}(\tilde{\sigma}_{\alpha,i} + \tilde{\sigma}_{\alpha,j}).\end{aligned} \tag{15}$$

2. Estimating the effective radial distribution function, $\tilde{\chi}_{ij}$

For a pure fluid the effective radial distribution function at contact of two segments of equal size, $\tilde{\chi}_i$, can be found from Wertheim's first-order thermodynamic perturbation theory (TPT1),[38,39] and can be written as the sum of a hard-sphere contribution and a chain contribution,

$$\tilde{\chi}_i = \tilde{\chi}_{\mathrm{HS},i} + \tilde{\chi}_{chain,i}. \tag{16}$$

The chain contribution, $\tilde{\chi}_{chain,i}$, arises due to the segments in the same chain screening each other from collisions. In the Carnahan and Starling[40] treatment of the hard-sphere system these contributions can be expressed as[20]

$$\tilde{\chi}_{\mathrm{HS},i} = \frac{1 - \frac{1}{2}\tilde{y}_{\chi,i}}{(1 - \tilde{y}_{\chi,i})^3}, \tag{17}$$

$$\tilde{\chi}_{chain,i} = -\frac{5}{8}\left(\frac{m_{\chi,i} - 1}{m_{\chi,i}}\right)\frac{1 - \frac{2}{5}\tilde{y}_{\chi,i}}{\left(1 - \frac{1}{2}\tilde{y}_{\chi,i}\right)(1 - \tilde{y}_{\chi,i})}, \tag{18}$$

where $\tilde{y}_{\chi,i} = (\pi/6)\,\tilde{\sigma}_{\chi,i}^3 m_{\chi,i} N_A \rho$ is the segment packing fraction. The radial distribution function does not go to unity in the low-density limit, as segments on the same chain screen each other from collisions with other segments, even at low density.

In order to estimate a segment diameter $\tilde{\sigma}_{\chi,i}$ and a chain length $m_{\chi,\,i}$ consistent with Eq. (16) an additional constraint is needed. To this end we impose the constraint that the distance between the end segments calculated using $\tilde{\sigma}_{\alpha,i}$ and $m_{\alpha,\,i}$, and $\tilde{\sigma}_{\chi,i}$ and $m_{\chi,\,i}$ are equal, namely,

$$\tilde{\sigma}_{\alpha,i}(m_{\alpha,i} - 1) = \tilde{\sigma}_{\chi,i}(m_{\chi,i} - 1). \tag{19}$$

This constraint ensures that the length of the backbone of the chain remains constant and that taking $m_{\alpha,\,i} = 1$, in the limit of a spherical molecule, ensures $m_{\chi,\,i} = 1$.

In order to infer the mixing rule for the interaction parameters $\tilde{\chi}_{ij}$, we have followed the approach described in SAFT-HS,[23,41,42] here generalised to describe mixtures of chains differing in the number and size of the hard spheres. The resulting expressions are given by

$$\tilde{\chi}_{ij} = \tilde{\chi}_{CS,ij}\left(\tilde{\chi}_{ij}^{(0)} + F(\tilde{\rho})\right) \tag{20}$$

$$\tilde{\chi}_{CS,ij} = \frac{1}{1 - \tilde{\xi}_3} + 3\left(\frac{\tilde{\sigma}_{\chi,i}\tilde{\sigma}_{\chi,j}}{\tilde{\sigma}_{\chi,i} + \tilde{\sigma}_{\chi,j}}\right)\frac{\tilde{\xi}_2}{(1 - \tilde{\xi}_3)^2} + 2\left(\frac{\tilde{\sigma}_{\chi,i}\tilde{\sigma}_{\chi,j}}{\tilde{\sigma}_{\chi,i} + \tilde{\sigma}_{\chi,j}}\right)^2\frac{\tilde{\xi}_2^2}{(1 - \tilde{\xi}_3)^3}, \tag{21}$$

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$$\tilde{\chi}_{ij}^{(0)} = 1 - \frac{1}{8}\left[\left(\frac{m_{\chi,i}-1}{m_{\chi,i}}\right)\left(\frac{\tilde{\sigma}_{\chi,j}^{3}+\frac{3}{2}\tilde{\sigma}_{\chi,i}\tilde{\sigma}_{\chi,j}^{2}}{\left(\frac{\tilde{\sigma}_{\chi,i}+\tilde{\sigma}_{\chi,j}}{2}\right)^{3}}\right)+\left(\frac{m_{\chi,j}-1}{m_{\chi,j}}\right)\left(\frac{\tilde{\sigma}_{\chi,i}^{3}+\frac{3}{2}\tilde{\sigma}_{\chi,j}\tilde{\sigma}_{\chi,i}^{2}}{\left(\frac{\tilde{\sigma}_{\chi,i}+\tilde{\sigma}_{\chi,j}}{2}\right)^{3}}\right)\right], \tag{22}$$

$$F(\tilde{\rho}) = \frac{\sum_{i,j}\tilde{x}_i\tilde{x}_j\left(\frac{\pi}{6}\left(\frac{\tilde{\sigma}_{\chi,i}+\tilde{\sigma}_{\chi,j}}{2}\right)^{3}\right)\tilde{\chi}_{CS,ij}\left(1-\tilde{\chi}_{ij}^{(0)}\right)+\frac{\tilde{Z}_{chain}}{4\tilde{\rho}}}{\sum_{i,j}\tilde{x}_i\tilde{x}_j\left(\frac{\pi}{6}\left(\frac{\tilde{\sigma}_{\chi,i}+\tilde{\sigma}_{\chi,j}}{2}\right)^{3}\right)\tilde{\chi}_{CS,ij}} \tag{23}$$

$$\tilde{Z}_{chain} = -\sum_i \tilde{x}_i\left(\frac{m_{\chi,i}-1}{m_{\chi,i}}\right)\left(\frac{\tilde{\xi}_3(1-\tilde{\xi}_3)+\frac{3}{2}\tilde{\sigma}_{\chi,i}\tilde{\xi}_2(1+\tilde{\xi}_3)+\frac{1}{2}\tilde{\sigma}_{\chi,i}^{2}\tilde{\xi}_2^{2}\left(\frac{2+\tilde{\xi}_3}{1-\tilde{\xi}_3}\right)}{(1-\tilde{\xi}_3)^2+\frac{3}{2}\tilde{\sigma}_{\chi,i}\tilde{\xi}_2(1-\tilde{\xi}_3)+\frac{1}{2}\tilde{\sigma}_{\chi,i}^{2}\tilde{\xi}_2^{2}}\right), \tag{24}$$

where the moment densities are defined as $\tilde{\xi}_m = (\pi/6) N_A \sum_i \tilde{\sigma}_{\chi,i}^{m} m_{\chi,i} x_i \rho$. More details are given in the Appendix, together with various mixing rules that are considered.

3. Estimating the zero-density parameters

In order to calculate the zero-density limit of the viscosity of free segments, $\tilde{\eta}_i^{(0)}$, we make use of Eq. (5) for each pure species. The interaction viscosity in the zero-density limit, $\tilde{\eta}_{ij}^{(0)}$, for each binary pair, is then given by

$$\tilde{\eta}_{ij}^{(0)} = \eta_{ij}^{(0)}\tilde{\chi}_{\alpha,ij}^{(0)}, \tag{25}$$

where $\tilde{\chi}_{\alpha,ij}^{(0)}$ is given by Eq. (22) using $\tilde{\sigma}_{\alpha,i}$ and $m_{\alpha,i}$ for consistency with Eq. (5).

E. Application to real mixtures

To perform an initial assessment of the accuracy of the newly developed VW-chain method, we limit our investigation to liquid mixtures consisting of *n*-alkane molecules. Although in the VW model different species are represented by homonuclear chains, whose segments can have different diameters, in this particular example, we represent each alkane molecule as a chain made up of equally sized "methane-like" segments. For this purpose, the diameter of a segment, $\tilde{\sigma}_\alpha$, is taken to be the effective diameter of methane at a given temperature, where methane is modelled as a single segment molecule. We have successfully used this concept in our previous work[20] to analyse the viscosity of pure normal alkanes. The effective diameter of methane, $\tilde{\sigma}_\alpha$, is obtained from Eq. (2), where the parameter α is evaluated from Eq. (13), which requires knowledge of the viscosity of pure methane at a given temperature. A figure showing $\tilde{\sigma}_\alpha$ as a function of temperature can be found in Ref. 20. For an *n*-alkane of carbon number C, the number of segments, m_α, is calculated from the formula $m_\alpha = 1 + (C-1)/3$ developed from consideration of the equilibrium thermodynamics,[41–43] that was also shown to be valid when analysing viscosity.[20] Once σ_α and m_α are known one can calculate $\tilde{\eta}_i^{(0)}$, $\tilde{\chi}_i^{(0)}$, and $\tilde{\alpha}_i$ for each alkane by means of Eqs. (5), (11), and (13), respectively. The calculation of $\tilde{\sigma}_\chi$ and m_χ for each alkane is slightly more intricate and it involves a simultaneous solution of Eqs. (16) and (19), where the value of effective radial distribution function is obtained from Eq. (11).

It is interesting to note that, unlike $\tilde{\sigma}_\alpha$ which is only a function of temperature, $\tilde{\sigma}_\chi$ is also a weak function of density. This is not surprising since $\tilde{\sigma}_\chi$ is evaluated from the effective hard-core radial distribution function, $\tilde{\chi}$, (see Eq. (16)), which is a function of density. This raises an interesting question, at what density should one evaluate $\tilde{\sigma}_\chi$? Or more to the point, given the molar density of the mixture, ρ, at what density should one evaluate the pure species parameters, so that they are representative of the interactions that the pure species undergo in a mixture? In the original VW method,[26,27] based on hard spheres, the mixing rule for the effective radial distribution function was written in terms of radial distribution functions for pure species and hence the molar density was an implied choice. However, this choice is unsuitable at liquid-like densities for mixtures of molecules that are very different in size. This difference in size makes the packing fraction very different for each species at the same molar density. Hence, such a pure fluid does not provide a good representation of the interactions of that particular species in the mixture. For this reason and given that the critical volume of a fluid is usually regarded as a measure of the hard-core volume, we have chosen to evaluate the required properties of the pure species at the same reduced density, ($\rho_r = \rho/\rho_{critical}$), as that of the mixture. For the purposes of this paper the critical density of the mixture was estimated by means of $\rho_{c,mix.} = [\sum x_i/\rho_{c,i}]^{-1}$. We will further examine the consequence of this density choice in Sec. III.

Once the pure species parameters, $\tilde{\sigma}_{\alpha,i}$, $m_{\alpha,i}$, $\tilde{\sigma}_{\chi,i}$, and $m_{\chi,i}$ have been evaluated one can evaluate all the mixture parameters by means of Eqs. (20)–(25) and subsequently the mixture viscosity by means of Eqs. (6)–(10). Therefore, to evaluate the viscosity of a liquid mixture of *n*-alkanes with the VW-chain method one only requires a knowledge of the viscosity of pure species and two temperature-dependent, dilute-gas binary parameters, $\eta_{ij}^{(0)}$ and A_{ij}^{*}. For the purpose of this work $\eta_{ij}^{(0)}$ and A_{ij}^{*} are obtained from standard references,[35,36] while the sources of pure species viscosity are discussed in Sec. III.

III. RESULTS AND DISCUSSION

In order to illustrate the predictive power of the VW-chain method and to investigate some of the assumptions made in deriving it, we examine two examples in detail. One, a (*n*-octane + *n*-dodecane) mixture made up of long

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chain-like molecules and the other, a (methane + *n*-decane) mixture consisting of spherical and long chain-like molecules. For both of these mixtures the original VW method, which is based on representing molecules as effective hard spheres, failed to provide an accurate description of the liquid viscosity.

There exist accurate sets of experimental data, for both mixtures, that in this study we use as a benchmark. In his Ph.D. thesis, Caudwell[44] reported viscosity and density measurements for two liquid mixtures of (*n*-octane + *n*-dodecane) ($x_{\text{octane}} = 0.434$ and $x_{\text{octane}} = 0.743$), at three temperatures from 323.15 to 423.15 K and pressures up to 200 MPa with a quoted uncertainty of 2%. Audonnet and Padua[45] have measured the viscosities and densities of (methane + *n*-decane) mixtures using a vibrating-wire technique with a quoted uncertainty of 3%. These measurements cover a temperature range from 303.15 to 393.15 K and pressures up to 75 MPa.

The VW-chain method requires knowledge of the pure-species viscosity. The viscosity of pure methane is obtained from Quinones-Cisneros *et al.*[46] as implemented in REFPROP V8. In the temperature and density range of interest in our work the claimed uncertainty of the correlation ranged from 2% to 5%. The correlations of Huber *et al.*[47,48] are used to estimate the viscosity of the *n*-octane, *n*-decane, and *n*-dodecane. The uncertainty of these correlations is between 2% and 3%. The correlations reproduce Caudwell's pure-species viscosity data with deviations ranging from −4.2% to +0.6% for *n*-octane and from −1.5% to +4.9% for *n*-dodecane, while the pure *n*-decane data of Audonnet and Padua is reproduced with a deviation ranging from −2.5% to 0.7%.

The percentage deviations of the VW-chain predicted data from the experimental data for the (*n*-octane + *n*-dodecane) mixture is illustrated in Fig. 1. The experimental data are reproduced with an absolute average deviation (AAD) of 1.3% and maximum absolute deviation of 3.5%. No trends in temperature or density could be discerned. Taking into account the uncertainty of pure species correlations and the quoted experimental uncertainty of the data, the agreement can be deemed to be very good.

The percentage deviation for the (methane + *n*-decane) mixture is shown in Fig. 2. The deviations are larger than for the (*n*-octane + *n*-dodecane) mixture, with an AAD of 5.4% and maximum absolute deviation of 14%. There is a strong trend with density which indicates that further refinement of VW-chain model is necessary for highly asymmetric alkane mixtures of this type. However, it should be pointed out that the viscosity of this mixture exhibits a very strong, non-linear increase with increasing composition of *n*-decane which makes accurate predictions rather difficult. For instance at a mixture density of 742.4 kg/m^3 the viscosity of pure *n*-decane is approximately five times larger than that of pure methane, at the same reduced density.

A number of assumptions have been made in developing the VW-chain method. We investigate the influence of some of the assumptions on the overall agreement between the predicted and experimental data and report the results for the (methane + *n*-decane) mixture only, as the (*n*-octane + *n*-dodecane) system appeared to exhibit similar qualitative behaviour. An assessment of the use of different mixing rules (see Appendix) on predictive capability of VW-model is illustrated in Fig. 3. Although there are differences of the order of 5% between different sets of mixing rules the general trend is to shift the deviations, but not affect the density trend already observed for this mixture. The difference between the predictions with mixing rules 1–3 and 4–5 appears to decrease with a decrease in the asymmetry of the mixture and for the (*n*-octane + *n*-dodecane) mixture it is less than 1%.

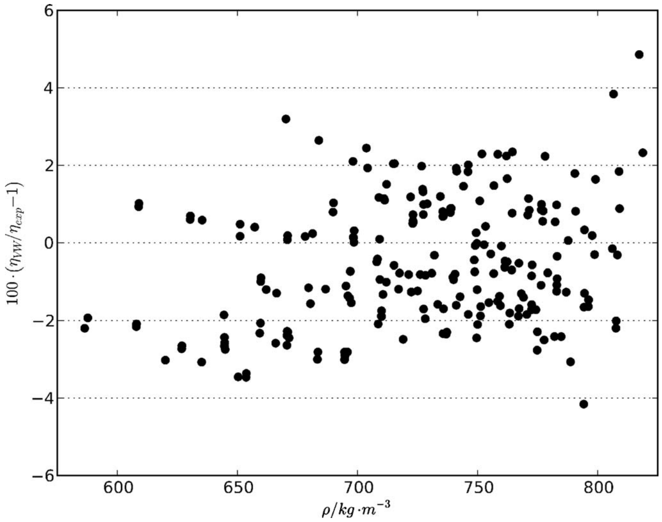

FIG. 1. Viscosity deviations obtained with the VW method for chain molecules developed here from the experimental data for (*n*-octane + *n*-dodecane) of Caudwell (Ref. 44).

The effect of evaluating the pure species properties at the molar, mass, and reduced density of the mixture is demonstrated in Fig. 4. The results for molar density indicate a two order of magnitude over-prediction. Furthermore, evaluating pure species properties at the molar density of the mixture requires properties of the heavier species at unrealistically high densities, where either of the pure species is solid or there are no viscosity correlations available. Although the deviations

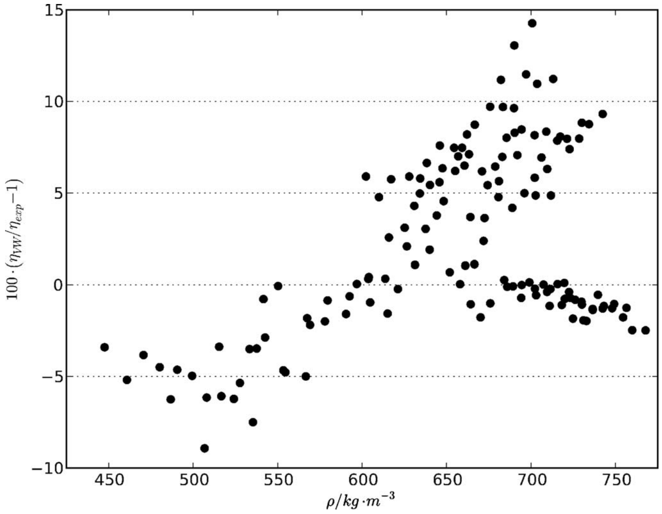

FIG. 2. Viscosity deviations obtained with the VW method for chain molecules developed here from the experimental data for (methane + *n*-decane) of Audonnet and Padua (Ref. 45).

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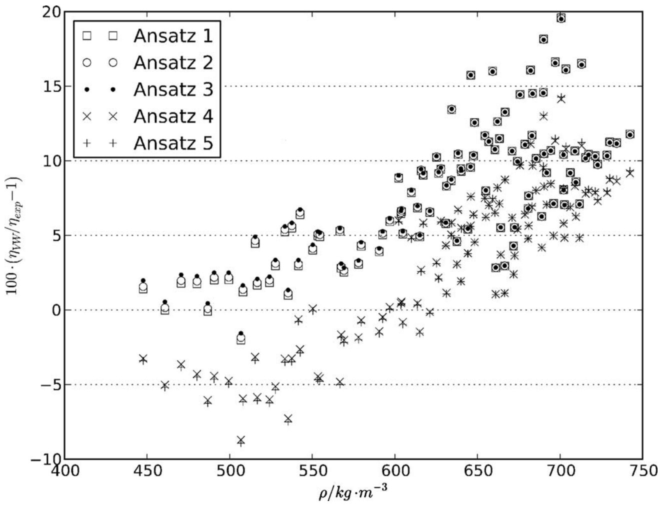

FIG. 3. Viscosity deviations obtained with the VW method for chain molecules developed here from the experimental data for (methane + *n*-decane) of Audonnet and Padua (Ref. 45) using: Eq. (A10), Ansatz 1; Eq. (A11), Ansatz 2; Eq. (A12), Ansatz 3; Eq. (A13), Ansatz 4; and Eq. (A14), Ansatz 5.

decrease with a decrease in the asymmetry of the mixture, this choice of density is unsuitable for application in the liquid state. This is not surprising since the molar density will result in a large overestimation of collision rate for heavier species, that unduly influences the collision rate between unlike species. The choice of either mass or reduced density would appear to offer a better description of the overall collision rate. As illustrated in Fig. 4, the choices of mass and reduced density result in similar deviations. However, evaluating pure species properties at the mass density of the mixture requires properties of the lighter species at unrealistically high densities, thus limiting its applicability.

We have refrained in this work from examining the role that the connectivity of the segments in a chain plays in determining the viscosity. Although one could, for this purpose, form a fluid of disconnected segments, the VW model, in its present form, cannot be used to estimate the viscosity of such a fluid. In the VW method, one evaluates the effective size (and shape) of the species from the viscosity of each pure species. In doing so, one postulates that the molecules can be represented as chains of connected segments whose effective parameters, $\tilde{\sigma}_\chi$ and m_χ, are obtained from the viscosity. Although for alkane mixtures, presented in this work, one represents a segment as having a "methane-like" effective diameter $\tilde{\sigma}_\alpha$, the mass of segment is given by $\tilde{M} = M_{alkane}/m_\alpha$. Hence, if we were to break up the chain to form a fluid consisting of disconnected segments, there is no equivalent pure fluid to be used as the source of viscosity for $\tilde{\sigma}_\chi$ and m_χ. Nevertheless the comparison of the high-density limit of the radial distribution function at contact for chains with that for spheres, Eqs. (16)–(18), does confirm the intuitive expectation that the connectivity of chain molecules has less impact at high density.

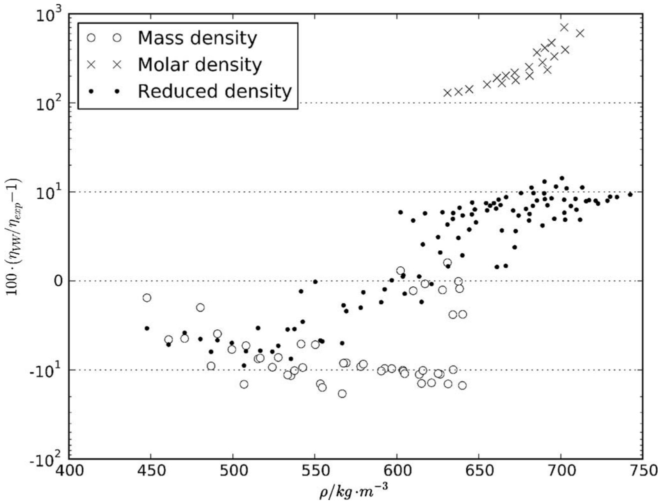

FIG. 4. Viscosity deviations of obtained with the VW method for chain molecules developed here from the experimental data for (methane + *n*-decane) of Audonnet and Padua (Ref. 45) when the properties of the pure species are evaluated at the molar, mass, and reduced density of the mixture.

IV. CONCLUSIONS

The VW method, that used to predict the viscosity of dense fluid mixtures made up of molecules represented as hard spheres, has been extended in this work to predict the viscosity of liquid mixtures consisting of chain-like molecules. This was achieved by postulating that the molecules can be represented as chains made up of hard, spherical segments that undergo instantaneous collisions. The new expressions for the viscosity of liquid mixtures were subsequently derived by extending the Enskog-Thorne approach to chain-like molecules. For realistic fluids at liquid-like densities, the resulting description suffers from the same deficiencies as the original Enskog's theory. In particular, it cannot be used to predict *a priori* the viscosity from the knowledge of the size and shape of the molecules. However, following the original VW method, we showed in the present work that it is possible to assign the molecular size and shape to each species in the mixture from knowledge of its viscosity. One of the consequences of using the effective molecular parameters is that one needs to distinguish between effective size of the molecule for the collisional dynamics and that for the excluded volume. By making an additional constraint that ensures that the length of the backbone of the chain remains constant we can describe the molecules of each pure species by three effective parameters; namely two diameters, one for collision dynamics and one for excluded volume, and the number of segments in the chain.

In order to calculate the viscosity of a mixture, we need to relate the effective parameters of the pure species to those for the like and unlike binary interactions. We have chosen to do so at the level of excluded volumes and radial distribution functions and consequently we have developed mixing rules for these two quantities. The mixing rule for excluded volume is relatively straightforward and is based on geometric considerations that include the mutual excluded volume of two spherocylinders and the assumption that the excluded volume of two spheres can be obtained by using an average diameter. In the limit of zero density it is possible to derive

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the thermodynamically consistent mixing rule for the radial distribution function and we have done so by following the SAFT approach. At finite density the present theory does not allow us to uniquely determine the chain contribution. Hence, we have postulated a number of possible *Ansätze* regarding the approximate density behaviour of the chain contribution. At present, it is only at the level of validation of the VW-chain method where one could distinguish between different possibilities.

The newly developed VW-chain model has been presented for the prediction of the viscosity of liquid mixtures. It is founded on the kinetic theory, modified to take into account the behaviour of real fluids, and on a set of thermodynamically consistent mixing rules. The model has no adjustable parameters, and requires no dense mixture viscosity data. The VW-chain model has been tested by comparing its predictions with the experimental viscosity data for the (*n*-octane + *n*-dodecane) and the (methane + *n*-decane) mixtures, i.e., mixtures made up of long, chain-like molecules and mixtures consisting of spherical and long chain-like molecule. The experimental data for the (*n*-octane + *n*-dodecane) mixture are reproduced with an AAD of 1.3% and maximum absolute deviation of 3.5%, while for the (methane + *n*-decane) mixture the AAD was 5.4% and maximum absolute deviation was 14%. This illustrates that the newly developed VW–chain model is capable of accurately representing the viscosity of real liquid mixtures.

We are currently undertaking a more encompassing validation of the VW-chain method and will shortly report on its ability to predict the viscosity of a plethora of *n*-alkane mixtures. In future work we intend to examine the explicit effect of attractive interactions on the viscosity of chain molecules within a full SAFT-VR treatment[43,49] for systems with hard-core segments interacting via variable range square-well,[43] Yukawa[50] or soft-core[51,52] interactions.

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APPENDIX: THE RADIAL DISTRIBUTION FUNCTION OF CHAIN MIXTURES

In this appendix, we derive a mixing rule for the segment collision rate parameters, $\tilde{\chi}_{ij}$. The factor χ was originally introduced by Enskog[11,12] to correct the probability of collision in dense fluids made up of hard spheres. From the Clausius virial expression for the pressure, it is possible to prove that, in the thermodynamic limit, χ converges to the radial distribution function at contact. Here, following the approach presented in our previous work,[20] we assume this link is still valid for chain molecules and define an effective radial distribution function at contact per segment, $\tilde{\chi}_{ij}$. As discussed in Sec. II B, within the dense region, a fluid consisting of a mixture of chain molecules is modelled as a fluid of hard spheres of various diameters. By means of the compressibility factor, an equation is obtained for a sum of all $\tilde{\chi}_{ij}$ and further equations are found for the zero-density limits of $\tilde{\chi}_{ij}^{(0)}$. Finally, a simple Ansatz is made in order to infer the density-dependence of $\tilde{\chi}_{ij}$.

The compressibility factor of a chain molecule mixture, $\tilde{Z}$, can be used to define an effective radial distribution function, $\tilde{\chi}_{ij}$, using the pressure equation,[53]

$$\tilde{Z} \equiv 1 + 4\tilde{\rho} \sum_{i,j} \tilde{x}_i \tilde{x}_j \left(\frac{\pi}{6} \left(\frac{\tilde{\sigma}_i + \tilde{\sigma}_j}{2} \right)^3 \right) \tilde{\chi}_{ij}. \tag{A1}$$

Furthermore, the Helmholtz free energy can be expressed as

$$A = A_{\mathrm{HS}} + A_{chain} = A_{\mathrm{HS}} + \sum_i N_i \left(m_i - 1\right) a_{ii}, \tag{A2}$$

where the index i runs over all the species. A_{HS} is the Helmholtz free energy of the hard-sphere contribution to the mixture. N_i and m_i are the number of molecules and segments per molecule for species i, and a_{ii} is the free energy change due to the bonding of two adjacent segments belonging to a given molecule of species i.

By differentiating Eq. (A2) with the respect to the volume we can obtain the compressibility factor. Hence, we define that

$$\tilde{Z} = \tilde{Z}_{\mathrm{HS}} + \tilde{Z}_{chain}, \tag{A3}$$

$$\tilde{\chi}_{ij} \equiv \tilde{\chi}_{\mathrm{HS},ij} + \tilde{\chi}_{chain,ij}, \tag{A4}$$

where $\tilde{Z}_{\mathrm{HS}}$ is the compressibility factor for a mixture of free hard spheres and $\tilde{\chi}_{\mathrm{HS},ij}$ is the radial distribution function at contact of free hard spheres of species i and j.

$\tilde{Z}_{chain}$ is the contribution due to the segment bonding in the chains and can be written as[23]

$$\begin{aligned}\tilde{Z}_{chain} &= \frac{\tilde{\rho}}{\tilde{N} k_B T} \left(\frac{\partial A_{chain}}{\partial \tilde{\rho}} \right)_T \\ &= \frac{\tilde{\rho}}{k_B T} \sum_i \tilde{x}_i \left(\frac{m_i - 1}{m_i} \right) \left(\frac{\partial a_{ii}}{\partial \tilde{\rho}} \right)_T,\end{aligned} \tag{A5}$$

where $\tilde{N} = \sum_i N_i m_i$ is the number of segments in the mixture. $\tilde{Z}_{\mathrm{HS}}$ is defined as

$$\tilde{Z}_{\mathrm{HS}} = 1 + 4\tilde{\rho} \sum_{i,j} \tilde{x}_i \tilde{x}_j \left(\frac{\pi}{6} \left(\frac{\tilde{\sigma}_i + \tilde{\sigma}_j}{2} \right)^3 \right) \tilde{\chi}_{\mathrm{HS},ij}. \tag{A6}$$

In order to estimate the free energy contribution due to bonding, a_{ii}, one can consider an associating mixture of monomers in the limit of complete association, corresponding to the TPT1 approximation.[23,38] The chemical potential due to the formation of each bond at infinite dilution is given exactly[54,55] by $-k_B T \ln \tilde{\chi}_{\mathrm{HS},ij}$, and, as is common in SAFT approaches, the cost in free energy per bond per molecule for the fully bonded chain fluid can thus be approximated as

$$a_{ii} = -k_B T \ln \tilde{\chi}_{\mathrm{HS},ii}, \tag{A7}$$

which essentially defines $\tilde{\chi}_{\mathrm{HS},ii} = \exp\left(-a_{ii}/k_B T\right)$ as the contact value of the potential of mean force, first introduced by Kirkwood.[56]

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Combining Eqs. (A1) and (A3)–(A7) yields an equation for a weighted sum of $\tilde{\chi}_{chain,ij}$ in terms of chain lengths and hard-sphere parameters, namely

$$\sum_{i,j}\tilde{x}_i\tilde{x}_j\left(\frac{\pi}{6}\left(\frac{\tilde{\sigma}_i+\tilde{\sigma}_j}{2}\right)^3\right)\tilde{\chi}_{chain,ij} = -\frac{1}{4}\sum_{i}\tilde{x}_i\left(\frac{m_i-1}{m_i}\right)\left(\frac{\partial\ln\tilde{\chi}_{\mathrm{HS},ii}}{\partial\tilde{\rho}}\right). \tag{A8}$$

$\tilde{\chi}_{\mathrm{HS},ii}$ can be estimated using the extensions of the Carnahan and Starling expression[40] to mixtures[57,58] which is given by Eq. (21). In order to solve Eq. (A8) for $\tilde{\chi}_{chain,ij}$ we first examine the zero-density limit.

When two segments are on trajectories that lead to a collision, a third segment near one of the segments may collide with it before, thus screening the original collision. $\tilde{\chi}_{chain,ij}$ incorporates the effect of this screening of collisions between species i and j by other segments, including those of the same species and the same chain. The probability of finding two segments near to each other, so that one can screen the collision of the other, is non-zero even in the low-density limit, because the neighbouring segments in the same chain are always close. Screening, therefore, also happens in the low-density limit, and $\tilde{\chi}^{(0)}_{chain,ij} = \lim_{\rho\to 0}\tilde{\chi}_{chain,ij}$, is non-zero. However, as the probability of finding two chains in close proximity does vanish in the low-density limit, screening of collisions between segments of two species can only occur in the low-density limit due to segments of either of the same two species, and not those of any third species. This means that all other species can be ignored and in order to determine $\tilde{\chi}^{(0)}_{chain,ij}$ one can simply consider a binary mixture of species i and j.

For collisions between segments of species i with other segments of species i, the radial distribution function at contact is equal to that of a pure fluid of species i,

$$\tilde{\chi}^{(0)}_{chain,ii} = \tilde{\chi}^{(0)}_{chain,i}, \tag{A9}$$

which can be found from Eq. (18). Furthermore, for a binary mixture, $\tilde{\chi}_{chain,ij} = \tilde{\chi}_{chain,ji}$, and thus $\tilde{\chi}^{(0)}_{chain,ij}$ is uniquely determined by Eq. (A8) for a binary mixture of species i and j. By substituting Eq. (A7), and rearranging terms, one thus obtains Eq. (22) that is independent of segment fractions. This is consistent with a low-density virial expansion where only pair terms will contribute to the pressure of the system. By analogy with the virial expansion, we can also obtain Eq. (22) by simply assuming that $\tilde{\chi}^{(0)}_{chain,ij}$ is not a function of composition. Equation (22) obtained in this manner is not limited to binary mixtures, but it is valid for any multicomponent mixture.

However, the behaviour of $\tilde{\chi}_{chain,ij}$ at finite density is less easily understood; Eq. (A8) does not contain enough information to determine $\tilde{\chi}_{chain,ij}$ for higher densities. We therefore propose a simple Ansatz regarding the approximate behaviour of $\tilde{\chi}_{chain,ij}$ with density. Several possibilities are assessed

$$\tilde{\chi}_{chain,ij} = \tilde{\chi}^{(0)}_{chain,ij} + F(\tilde{\rho}), \tag{A10}$$

$$\tilde{\chi}_{chain,ij} = \tilde{\chi}^{(0)}_{chain,ij} + F(\tilde{\rho})\,\tilde{\chi}_{\mathrm{HS},ij}, \tag{A11}$$

$$\tilde{\chi}_{chain,ij} = \tilde{\chi}^{(0)}_{chain,ij} + F(\tilde{\rho})\left(\tilde{\chi}_{\mathrm{HS},ij} - \tilde{\chi}^{(0)}_{\mathrm{HS},ij}\right), \tag{A12}$$

$$\tilde{\chi}_{chain,ij} = \tilde{\chi}^{(0)}_{chain,ij}\tilde{\chi}_{\mathrm{HS},ij} + F(\tilde{\rho}), \tag{A13}$$

$$\tilde{\chi}_{chain,ij} = \left(\tilde{\chi}^{(0)}_{chain,ij} + F(\tilde{\rho})\right)\tilde{\chi}_{\mathrm{HS},ij}, \tag{A14}$$

where $F(\tilde{\rho})$ is a function of segment density only which can be determined from Eq. (A8). The results in the present work correspond to Ansatz in Eq. (A14) as shown in Eq. (20) and subsequent expressions. Additionally, at high densities the chain contributions tend to be relatively small compared to the hard-sphere terms. This means that for well-behaved systems, these *Ansätze* all produce very similar results.

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