SAFT-\(\gamma\) Force Field for the Simulation of Molecular Fluids. 5. Hetero-Group Coarse-Grained Models of Linear Alkanes and the Importance of Intra-molecular Interactions

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Abstract

The SAFT-\(\gamma\) Mie group-contribution equation of state [Papaioannou et al., J. Chem. Phys., 140, 054107 (2014)] is used to develop a transferable coarse-grained (CG) force-field suitable for the molecular simulation of linear alkanes. A hetero-group model is fashioned at the resolution of three carbon atoms per bead in which different Mie (generalized Lennard-Jones) interactions are used to characterize the terminal (\(\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}\)) and middle (\(-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-}\)) beads. The force field is developed by combining the SAFT-\(\gamma\) CG top-down approach [Avendaño et al., J. Phys. Chem. B, 115, 11154 (2011)] using experimental phase-equilibrium data for \(n\)-alkanes ranging from \(n\)-nonane to \(n\)-pentadecane to parametrize the inter-molecular (non-bonded) bead-bead interactions, and a bottom-up approach relying on simulations with the higher resolution TraPPE united-atom (UA) model [Martin and Siepmann, J. Phys. Chem. B, 102, 2569 (1998)] to establish the intra-molecular (bonded) interactions. The transferability of the SAFT-\(\gamma\) CG model is assessed from a detailed examination of the properties of linear alkanes ranging from \(n\)-hexane (\(n\)-C\(_6\)H\(_{14}\)) to \(n\)-octadecane (\(n\)-C\(_{18}\)H\(_{38}\)), including an additional evaluation of the reliability of the description for longer chains such as \(n\)-hexacontane (\(n\)-C\(_{60}\)H\(_{122}\)) and a prototypical linear polyethylene of moderate molecular weight (\(n\)-C\(_{900}\)H\(_{1802}\)). A variety of structural, thermodynamic, and transport properties are examined, including the pair distribution functions, vapour-liquid equilibria, interfacial tension, viscosity, and diffusivity. Particular focus is placed on the impact of incorporating intra-molecular interactions on the accuracy, transferability and representability of the CG model. The novel SAFT-\(\gamma\) CG force field is shown to provide a reliable description of the thermophysical properties of the \(n\)-alkanes, in most cases at a level comparable to the that obtained with higher resolution models.

1 Introduction

Molecular-dynamics and Monte Carlo computer simulation methods are very dependable techniques for studies of the structural and thermophysical and properties of real molecu-
lar systems provided that an appropriate force field is available to describe the interactions between the particles. The structural simplicity of alkanes coupled with their practical significance have lead to large body of simulation studies and the development of numerous reliable force fields\textsuperscript{1–5}. Linear alkanes constitute a convenient starting point for the development of force fields of more complex molecules such as macromolecules, polymers, and other compounds containing alkyl tails. As a result the development of models which are transferable for these classes of system over wide ranges of thermodynamic conditions and molecular weight continue to be a topic of significant interest.

Molecular models of alkanes traditionally invoke all-atom (AA)\textsuperscript{1,2}, united-atom (UA)\textsuperscript{3,4,6–9}, or anisotropic united-atom (AUA)\textsuperscript{5,10} representations. The AA level of resolution is clearly the more detailed and realistic, while the use of UA and AUA models reduces the number of interaction sites being considered resulting in an advantageous reduction in the overall computational overhead of the simulation\textsuperscript{4}. Popular and reliable UA force fields are now available for the representation of fluid-phase equilibria of hydrocarbons including, for example, the SKS\textsuperscript{6}, TraPPE\textsuperscript{4,7}, and NERD\textsuperscript{8} models, where the Lennard-Jones (12–6) potential is employed to treat non-bonded interactions between the UA beads. The Mie (\(n\)-6), generalized Lennard-Jones, potential has also been used to represent the the interactions between the UA beads in alkanes and perfluoroalkanes\textsuperscript{9}; a variation of the repulsive exponent (and range) of the potential allows for an improved description of the coexistence properties.

Force fields at the AA and UA level of resolution are well suited for the simulation of the thermophysical properties of systems comprising a few thousand small molecules, but are not practical in studies involving complex phenomena such as self-assembly and micro phase separation, or macromolecular particles that can contain hundreds of thousands of atoms and span the micrometer scale. Lower-resolution coarse-grained (CG) models, where the interaction sites (beads) are taken to incorporate larger numbers of atoms, offer a significant advantage for systems characterized by large length and time scales. The use of CG force fields is becoming increasingly popular in bridging the gap between the atomistic scale and
Within a CG formalism the interaction site comprising a group of atoms or functional groups is represented with an effective potential designed to retain an accurate description of the target properties of interest. CG force fields are computationally more efficient, allowing one to explore phenomena involving longer timescales over larger length scales\textsuperscript{11}. However, this computational gain is achieved at the expense of a loss in chemical resolution in the molecular model, loss of transferability over thermodynamic states and/or for different systems, and representability\textsuperscript{17,18}, whereby the properties of the system of interest cannot all be represented simultaneously.

The traditional procedure for the development of CG models is the so-called bottom-up approach whereby, once the level of resolution of the coarse graining (the number of atoms assigned per bead) is defined, information obtained at the more detailed molecular level is mapped at the less-detailed CG level\textsuperscript{19}. This type of bottom-up approach usually relies on knowledge of the structural and thermodynamic properties obtained from simulations of high-resolution AA or UA models, which serve as a reference target for the development of the coarser models\textsuperscript{20}. Key examples of bottom-up approaches include iterative Boltzmann inversion\textsuperscript{21,22} and force-matching methods\textsuperscript{19,23–25}. The former is based on matching pair correlation functions at both the atomistic and CG levels, while the latter relies on minimizing the differences between the forces acting on the CG sites and the corresponding forces on the reference atomic system.

The level of resolution of the coarse graining will have an effect on the accuracy of the description of a given property, as will the parameters characterizing the bonded and non-bonded interactions of the CG force field. The influence of different levels of resolution in the CG procedure has been recently assessed for different mapping schemes of \(n\)-alkanes (with \(\geq C_{12}\))\textsuperscript{26}. Taking \(n\)-dodecane as benchmark, one finds that as the degree of coarse gaining is increased (corresponding to models of progressively poorer resolution), the description of the thermodynamic properties deteriorates. It is known that CG models developed using
bottom-up approaches can suffer from a lack of representability which prevents one from capturing properties across different thermodynamic states, in part due to the fact that typically only a single thermodynamic state is used in the mapping. An improvement in the representability of the CG model can be obtained by using a multi-state iterative Boltzmann inversion scheme rather than the single-state method as has been demonstrated for the structural properties of \( n \)-dodecane\(^{27} \).

In top-down CG methods the parameters characterizing the CG force field are instead determined by direct optimization of the description of experimental observables. This type of approach has been used very successfully in the development of the MARTINI force field\(^{28,29} \), where the partitioning free energies between polar and apolar phases of a variety of chemical species are employed in the parametrization. A resolution of four heavy atoms per bead (referred to as a 4:1 mapping) is typically employed for the MARTINI CG force field, and the standard Lennard-Jones (12–6) potential is taken to represent the form of the non-bonded interaction between all of the beads. The bonded intra-molecular interactions of aliphatic hydrocarbon chains are obtained from an analysis of the angular distributions and configurational entropies of pure hydrocarbons in the liquid state using the UA GROMOS force field\(^{30} \) at the 4:1 level of resolution. A related parameterization for the \( n \)-alkanes at the 2:1 mapping level of resolution has recently been developed with the particle-swarm optimization technique\(^{31} \), where a good description of the heat of vaporization, the surface tension and the diffusion coefficient is demonstrated. The MARTINI force field is finding widespread use in simulation studies of biomolecular systems as a result of the group-contribution spirit of the approach which allows one to construct arbitrary molecules with off-the-shelf CG interaction parameters.

In this context it is important to mention the popular CG models of \( n \)-alkanes presented by Klein and co-workers\(^{32,33} \) which are also developed with both top-down and bottom-up approaches. In this case the non-bonded parameters are determined using target experimental data for the liquid density and surface tension, while the parametrization of the
bonded interactions is carried out using simulations at the atomistic scale. Chain molecules of various lengths were considered in the development of the force field but typically only at a single temperature. Of particular relevance to our current work is their use of the Mie ($\lambda_r - \lambda_a$) potential to represent the non-bonded interactions between the CG beads. By removing the constraint of a fixed repulsive exponent at the Lennard-Jones value of $\lambda_r = 12$, one can obtain an improved description of the macroscopic observables of interest. In the case of the $n$-alkanes a Mie (9–6) potential was employed to parametrized the CG interactions\textsuperscript{32}, and subsequently used to represent the aliphatic tail of phospholipid molecules\textsuperscript{33}.

A similar approach was later followed by Maerzke and Siepmann\textsuperscript{34} to develop a TraPPE-CG model for the $n$-alkanes in which the intra-molecular parameters were obtained using an iterative Boltzmann inversion procedure, and the inter-molecular interactions between CG beads, modelled with a potential of the Mie ($\lambda_r$–6) form, were parametrized using vapour-liquid coexistence data obtained from simulations of the corresponding TraPPE-UA model. The resulting force field was shown to provide an accurate description of the vapour-liquid equilibria for pure $n$-alkanes ranging from $n$-hexane to $n$-triacontane and for binary mixtures such as $n$-hexane + $n$-hexatriacontane.

These top-down approaches deliver CG models with much better transferability, but it is notable that the parameterization of the force field requires a number of computationally expensive molecular simulations to be carried out for intermediate systems characterized by suboptimal unbonded parameters, until the final set of parameters is obtained when the convergence criterion of the optimisation algorithm is met. A different approach based on the use of a free-energy function that explicitly takes into account the separate energetic and entropic contributions of the interactions has been proposed in order to improve the transferability of the models, using the linear $n$-alkane series as benchmark\textsuperscript{35}.

In addressing the challenge of developing CG models that are robust in terms of their transferability and representability, the use of an molecular-based equation of state (EOS) has been shown to present an distinct advantage\textsuperscript{36,37}. Providing the EOS yields a reliable and
accurate description of the macroscopic properties of the underlying molecular model used in the development of the CG representation, the algebraic formalism can be used to determine the non-bonded parameters of the force-field with minimal computational effort, allowing one to consider large sets of target experimental data simultaneously in the estimation of the model parameters. The statistical associating fluid theory (SAFT)\textsuperscript{38–42} framework provides a family of algebraic EOSs with a formal link between a detail molecular model and the thermodynamic properties of fluids of associating chain molecules. The PC-SAFT\textsuperscript{43} EOS was used early on\textsuperscript{44} to determine the non-bonded force-field parameters of \textit{n}-alkanes CG beads by tuning the model parameters to reproduce experimental data for the liquid density, enthalpy of vaporisation, and vapour pressure. The lack of a direct correspondence between the PC-SAFT model and the underlying force field required the use of an empirical iterative simulation procedure to refine the parameters of the model in order to provide simulated properties which are in sufficient agreement with the target experimental data. A reliable force field can nevertheless be obtained in this manner providing an accurate description of the coexistence densities, vapour pressure, and caloric properties of a number of \textit{n}-alkanes over a range of temperatures within just three simulation iterations. It should however be noted that because of the homonuclear nature of the underlying PC-SAFT model, different force-field parameters between the CG beads were obtained for each of the \textit{n}-alkanes studied.

The introduction of the Mie potential to represent the basis of the inter-molecular interactions between the molecular segments and the extension of the high-temperature perturbation expansion to third-order in the SAFT-VR Mie EOS\textsuperscript{45} provides a description of the thermodynamic properties of chain molecules formed from Mie beads which is of comparable accuracy to computer simulations for the underlying model. The use of an independent specification of the exponents describing the repulsive and attractive contribution of the Mie potential, allows for a versatile description of the inter-molecular interactions leading to a reliable description of the thermophysical properties, as demonstrated in a number of studies\textsuperscript{9,33,34,36,45–48}. The recasting of the SAFT-VR Mie formalism as the SAFT-\textgreek{gamma} Mie
group-contribution approach based on a heteronuclear model of molecules comprising Mie beads of different types (corresponding to different chemical functionality) has proved to be equally successful in terms of its applicability and accuracy in the description of the thermodynamic properties of a wide variety of systems and provides a framework to consider species with distinct chemical moieties explicitly. The development of CG models using a top-down methodology with the SAFT-γ Mie EoS, hereafter referred to as SAFT-γ CG force fields, has been presented in a series of contributions for a variety of molecular fluids including one-site models of carbon dioxide, homonuclear CG bead models of n-alkanes, greenhouse gases and refrigerants, natural gas condensates, water and aqueous mixtures, and heteronuclear models of aromatic compounds, polystyrene polymers, perfluoroalkylalkanes, and amphiphilic systems comprising nonionic, light-switching, and super spreading surfactants. The development and use of the SAFT-γ CG force fields in molecular simulation is reviewed in ref. A generalized methodology for the development of force field parameters for simple pure fluids based on a corresponding states approach has also been described.

The development of SAFT-γ CG force fields for n-decane (n-C_{10}H_{22}) and n-eicosane (n-C_{20}H_{42}) represented as homonuclear models with beads of equivalent size presented in ref. is of particular relevance to our current work. More specifically, the n-alkanes were modelled as chains of tangentially bonded identical spherical beads (three beads in the case of n-decane, and six beads in the case of n-eicosane), and, importantly, the chains were treated as fully-flexible; *i.e.*, no intra-molecular bond bending or torsional interactions were considered. Similarly, a homonuclear fully-flexible chain model was used to represent solutions of polystyrene in n-alkanes. The first-order thermodynamic perturbation theory (TPT1) of Werthiem which is the basis for the representation of the chain contribution in SAFT formalism, does not explicitly take into account the configurational structure and flexibility (or rigidity) of chain molecules. For relatively simple fluids, most of the macroscopic thermodynamic properties are quite insensitive to the precise description of the microscopic
molecular structure. This approximate treatment tends to break down, however, for more complex molecules such as amphiphiles or polymers, as is particularly apparent in the case of transport and interfacial properties.

The SAFT-\(\gamma\) CG force fields developed for fully flexible models of \(n\)-alkanes\(^{47}\) provide a good representation of the experimental fluid-phase equilibria (vapour pressure and saturated density) and vapour-liquid interfacial tension over a broad range of thermodynamic conditions, with larger deviations notable for the description of the vapour pressure at lower temperature, especially for the longer chains. An empirical rescaling of the inter-molecular parameters can be applied \textit{a posteriori} to improve the description of the saturation properties. It is, however, generally accepted that even in the case of relatively simple molecules such as \(n\)-alkane, a high-fidelity representation of force field incorporating both the inter-molecular and intra-molecular interactions (bond-stretching, bending, and torsional contributions) is required to reliably represent the physical properties of the system\(^{3-5}\).

In our current work we present the SAFT-\(\gamma\) CG force-field for \(n\)-alkanes based on hetero-nuclear beads at a resolution of three heavy atoms per bead (3:1 mapping), incorporating bonded as well as non-bonded interactions. We follow a a bottom-up approach to determine the characteristic constants of the bonded potential from UA simulations, and a top-down approach using the SAFT-\(\gamma\) Mie EOS to characterise the parameters of the non-bonded interaction using experimental fluid-phase coexistence data (saturated density and vapour pressure). We highlight the importance of the implementation of a hetero-segmented model in the development of a transferable force-field for linear alkanes. A detailed analysis of the impact of the inclusion of the bonded potential is presented. This contribution adds to our group’s body of work\(^{36,46,47,55,58-60}\) on the development of the SAFT-\(\gamma\) coarse-grained force field for the simulation of molecular fluids.

The paper is organized as follows: Details of the CG models are described in the next section, where the methodologies used to determine the parameters for both inter- and intra-molecular interactions are discussed. In Section 4 we present the results of molecular-
dynamics simulations for the structural, thermodynamic, and transport properties of a \( n \)-alkanes of varying chain length, including polyethylene chains of 300 CG beads (corresponding to a molecular weight of 12,602 g mol\(^{-1} \)), making appropriate comparisons with experimental data and the corresponding description with atomistic (UA) models. Our concluding remarks are summarised in Section 5. Details of the simulation methodology are provided in section 3.

![Figure 1: Heteronuclear SAFT-\( \gamma \) coarse-grained representation of \( n \)-nonane. Three backbone carbon atoms correspond to one CG bead (3:1 mapping scheme). The blue beads correspond to the (CH\(_3\)-CH\(_2\)-CH\(_2\)-) terminal (T) groups and the red bead to (-CH\(_2\)-CH\(_2\)-CH\(_2\)-) middle (M) group.](image)

## 2 Parametrization of SAFT-\( \gamma \) Mie coarse-grained force field

### 2.1 Inter-molecular interactions

We consider heteronuclear (hetero-group) segmented chain molecules formed from tangential spherical beads of different types. The interaction between two beads \( k \) and \( l \) is represented with the Mie potential,

\[
u_{kl}^{\text{Mie}}(r_{kl}) = C_{kl} \varepsilon_{kl} \left[ \left( \frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{kl}} - \left( \frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{kl}^a} \right],
\]

where \( r_{kl} \) is the centre-centre inter-bead distance, \( \varepsilon_{kl} \) the well depth of the potential, \( \sigma_{kl} \) the diameter of the bead, \( \lambda_{kl}^r \) the exponent controlling the hardness/softness of the repulsive
contribution, and $\lambda^a_{kl}$ the exponent controlling the range of the attractive contribution of the interaction. The constant $C_{kl}$ is defined as

$$C_{kl} = \frac{\lambda^r_{kl}}{\lambda^r_{kl} - \lambda^a_{kl}} \left( \frac{\lambda^a_{kl}/(\lambda^r_{kl} - \lambda^a_{kl})}{\lambda^r_{kl} - \lambda^a_{kl}} \right),$$

(2)

to ensure that the energy at the minimum of the potential is $-\varepsilon_{kl}$ irrespective of the values of the repulsive and attractive exponents.

As depicted in Figure 1 in the case of $n$-nonane, a 3:1 level of CG resolution is implemented, in which three consecutive backbone carbon atoms (with the corresponding bonded hydrogen atoms) are modelled as one CG bead. In our heteronuclear model two types of CG beads are used corresponding to either terminal (T) beads, representing (CH$_3$-CH$_2$-CH$_2$-) groups or middle (M) beads, representing (-CH$_2$-CH$_2$-CH$_2$-) groups.

The non-bonded inter-molecular parameters of the force field are estimated using the SAFT-$\gamma$ Mie group contribution EOS$^{49}$, carrying out a minimization of an objective function $F_{\text{obj}}$ based on the unweighed square residuals of experimental data (exp) and the corresponding SAFT-$\gamma$ Mie EoS description (cal) for the chosen properties. As is common practice in engineering applications we use the vapour (saturation) pressure and saturated-liquid density data over a wide range of temperatures as target properties. The objective function is given as

$$F_{\text{obj}}(\{T_q\}; \alpha) = \sum_{i=1}^{N_G} \left[ \sum_{q=1}^{N_{P_v,i}} \left( \frac{P_{cal}^{v,i}(T_q; \alpha) - P_{exp}^{v,i}(T_q)}{P_{exp}^{v,i}(T_q)} \right)^2 \right] + \sum_{q=1}^{N_{\rho_l,i}} \left( \frac{\rho_{cal}^{l,i}(T_q; \alpha) - \rho_{exp}^{l,i}(T_q)}{\rho_{exp}^{l,i}(T_q)} \right)^2,$$

(3)

where $N_{P_v}$ and $N_{\rho_l}$ are the number of experimental data points for the vapour pressure $P_v$ and the saturated-liquid density $\rho_l$ of compound $i$, respectively. The vector of SAFT parameters at the corresponding temperature $T$ of data point $q$ is represented by $\alpha = [\sigma_{kl}, \varepsilon_{kl}, \lambda^r_{kl}, \lambda^a_{kl}]$. 
The attractive range is fixed as \( \lambda_{kl}^a = 6 \) in all cases to reflect the London-type dispersion interaction characteristic of these non-polar systems.

The inter-molecular parameters of our heteronuclear model are based on the analysis of data for several \( n \)-alkanes, so that a unique set of parameters will, in principle, be transferable to other \( n \)-alkanes. While data for an arbitrary number of \( n \)-alkanes could be used, here we consider \( n\text{-C}_9\text{H}_{20} \), \( n\text{-C}_{12}\text{H}_{26} \) and \( n\text{-C}_{15}\text{H}_{32} \) as the target compounds in the parameter estimation. In this way one can ensure that the shortest chain (\( n \)-hexane \( n\text{-C}_6\text{H}_{14} \), which comprised only two terminal CG beads) and longer \( n \)-alkanes, for which the experimental data is less reliable, do not bias the resulting model.

The estimated SAFT-\( \gamma \) CG inter-molecular parameters are presented in Table 1. The parameters for like interactions including the diameters, dispersion energy, and repulsive exponents of the terminal-terminal and middle-middle bead interactions (\( \sigma_{TT}, \sigma_{MM}, \varepsilon_{TT}, \varepsilon_{MM}, \lambda_{TT} \) and \( \lambda_{MM} \)) as well as the unlike terminal-middle bead dispersion energy (\( \varepsilon_{TM} \)) are estimated by minimization of the the objective function given in Equation 3. The thermodynamic conditions and source of the experimental vapour-liquid equilibrium (VLE) data considered are presented in Table 2. The unlike parameters for the diameter \( \sigma_{TM} \) and range \( \lambda_{TM}^r \) of the model are determined using combining rules:

\[
\sigma_{kl} = \frac{\sigma_{kk} + \sigma_{ll}}{2} \quad \text{(4)}
\]

and

\[
\lambda_{kl}^r - 3 = \sqrt{(\lambda_{kk}^r - 3)(\lambda_{ll}^r - 3)} \quad \text{(5)}
\]

The deviation of the description obtained with the SAFT-\( \gamma \) Mie EoS (cal) using the parameters presented in Table 1 in comparison to experimental (exp) data is presented in Table 2, in terms of the percentage average absolute deviation \%AAD, which is determined as

\[
%\text{AAD}_j = \frac{1}{N_{X_j}} \sum_{i=1}^{N_{X_j}} \left| \frac{X_{j,i}^{\text{exp}} - X_{j,i}^{\text{cal}}}{X_{j,i}^{\text{exp}}} \right| \times 100, \quad j = \{ P_v, \rho_l \} \quad \text{(6)}
\]
Table 1: SAFT-γ CG Mie inter-molecular force-field parameters for beads of type T (terminal, CH₃-CH₂-CH₂- groups) and type M (middle, -CH₂-CH₂-CH₂- groups) for n-alkanes: σ_{kl} is the bead diameter, ε_{kl} the well depth of the potential, and λ_{rkl} the repulsive exponent of the potential. The attractive exponent λ_{akl} = 6 is fixed to the London value in all cases. The unlike parameters σ_{TM} and λ_{rTM} are determined using the combining rules defined in Equations 4 and 5, while ε_{TM} is estimated by minimization of Eq. 3 using the SAFT-γ Mie EoS. k_B corresponds to the Boltzmann constant.

| Type k | Type l | σ_{kl}/Å | λ_{rkl} | (ε_{kl}/k_B)/K |
|--------|--------|----------|---------|----------------|
| M      | M      | 4.1840   | 16.433  | 377.14         |
| T      | T      | 4.5012   | 15.947  | 358.37         |
| T      | M      | 4.3426   | 16.188  | 345.72         |

where N_{Xj} is the number of data points of a given property X_j.

Table 2: Percentage average absolute deviations (%AAD) for the vapour pressure P_v(T) and saturated-liquid density ρ_l(T) obtained with the SAFT-γ Mie equation of state and the CG model of Table 1 for selected n-alkanes. The asterisk indicates that experimental data for n-C_{6}H_{14} and n-C_{18}H_{38} were not included in the parameter estimation; the calculations in this case are predictive.

| Compound | T_{range}/K | Ref. | %AAD ρ_l(T) | %AAD P_v(T) |
|----------|-------------|------|-------------|-------------|
| n-C_{6}H_{14} | 178–458      | 72   | 1.50        | 17.80       |
| n-C_{9}H_{20}  | 220–580      | 72   | 0.45        | 0.55        |
| n-C_{12}H_{26} | 264–584      | 72   | 1.05        | 2.55        |
| n-C_{15}H_{32} | 285–625      | 73   | 1.18        | 3.27        |
| n-C_{18}H_{38} | 305–645      | 74   | 2.93        | 12.87       |

The overall %AAD for the properties of the three target n-alkanes used in the parameter estimation of the SAFT-γ Mie CG force field (n-C_{9}H_{20}, n-C_{12}H_{26} and n-C_{15}H_{32}) are found to be small: 0.89 for the saturated-liquid density and 2.12 for the vapour pressure, confirming the adequacy in terms of accuracy and transferability of the equation of state and CG non-bonded force-field parameters proposed here. As a point of comparison it is also useful to consider the homonuclear (all beads are identical) SAFT-γ CG force field for linear alkanes presented in other work. The use of a homonuclear model leads to slightly smaller deviations in comparison with experimental data (the overall %AAD for the same compounds with the CG force field determined in ref. 58,61 is 0.41 for the saturated-liquid...
density 2.44 and for vapour pressure) but the approach has the disadvantage of not being transferable from one compound to another; each \( n \)-alkane is modelled with a different set of non-bonded parameters, meaning that these cannot be used in a predictive manner for \( n \)-alkanes of arbitrary chain length. The corresponding-states parametrization presented in ref.\(^{54,64}\) suffers from the same limitation of lack of transferability. A heteronuclear model such as the one developed here leads to the characterization of the different bead-bead interaction parameters, much as in the spirit of the popular UA TraPPE\(^7\), NERD\(^8\), and CG MARTINI\(^{29}\) force fields. Once the bead-bead parameters are determined, \( n \)-alkanes of arbitrary chain length can be considered. Furthermore, the heteronuclear force fields for the individual beads characterized here can also be used to model other classes of compounds containing these groups.

The transferability of our SAFT-\( \gamma \) Mie CG model is further assessed for the prediction of properties of compounds which were not included in characterising the force-field parameters. The fluid-phase equilibria is determined with the SAFT-\( \gamma \) Mie EoS for \( n \)-C\(_6\)H\(_{14}\) and \( n \)-C\(_{18}\)H\(_{38}\) using the optimized parameters given in Table 1 and the corresponding \%AADs are also provided in Table 2. For these two compounds the deviations are found to be slightly larger, especially in the case of the predicted vapour pressures. To a certain extent, the tangent-bead model developed here limits our ability to provide a very accurate description of the vapour pressure for a large range of linear alkanes\(^{74}\), although it is important to note also that the vapour pressures of long \( n \)-alkanes are very low and that a more appropriate measure of the performance of the would be in absolute and not relative terms; we use such a measure for comparison of vapour pressure data later in the current work.
2.2 Intra-molecular interactions

The intra-molecular interactions are described with harmonic potentials for both bond stretching and angle bending:

\[
\frac{U_{\text{intra}}}{k_B} = \sum_{\text{bonds}} \frac{1}{2} \frac{k_{\text{bond}}}{k_B} (r - r_0)^2 + \sum_{\text{angles}} \frac{1}{2} \frac{k_{\text{angle}}}{k_B} (\theta - \theta_0)^2
\]

(7)

where \(k_{\text{bond}}\) and \(k_{\text{angle}}\) are the stretching (bond) and bending (angle) constants, respectively, \(r_0\) and \(\theta_0\) are the equilibrium bond length and bond angle, respectively, and \(k_B\) is the Boltzmann constant. The dihedral contribution to the intra-molecular potential is not been included in the force field, as magnitude of the torsional term is found to be lower than \(k_B T\).

Non-bonded interactions between pairs of beads separated by more than three bonds are considered.

The intra-molecular potential parameters are obtained by carrying out molecular dynamics (MD) simulations using the TraPPE-UA force field\(^4\) for \(n\)-C\(_6\)H\(_{14}\), \(n\)-C\(_9\)H\(_{20}\), and \(n\)-C\(_{12}\)H\(_{26}\) at a number of thermodynamic conditions (cf. Table 3). We note here that simulations using the NERD-UA force field\(^75\) would lead to very similar results as the intra-molecular parameters are identical to those employed in the TraPPE-UA model. A preliminary evaluation of the intra-molecular parameters of the \(n\)-alkanes for gas and liquid states at two states (400 and 600 K) lead to values of \(k_{\text{bond}}/k_B = 7373\) K/Å\(^2\) \((r_0 = 3.50\) Å\)) and \(k_{\text{angle}}/k_B = 2124\) K/rad\(^2\) \((\theta_0 = 159.9^\circ)\) when obtained at a temperature of 400 K, and \(k_{\text{bond}}/k_B = 7588\) K/Å\(^2\) \((r_0 = 3.50\) Å\)) and \(k_{\text{angle}}/k_B = 2668\) K/rad\(^2\) \((\theta_0 = 157.6^\circ)\) when averaged for states at 400 K and 600 K. These preliminary values of the intra-molecular interactions for the \(n\)-alkanes have already been used in some studies with the SAFT-\(\gamma\) Mie CG force-fields of chain molecules\(^{58,60}\).

A detailed examination of the intra-molecular parameters is provided over a range of temperatures for gas and liquid states densities (chosen to avoid any possibility of metastability) to improve the transferability of the resulting force filed. Subcritical gas and liquid states
Table 3: Thermodynamic density ($\rho$) and temperature ($T$) states and intra-molecular parameters (bond distance $r_0$, bond stretching constant $k_{\text{bond}}$, angle $\theta_0$, and bond bending constant $k_{\text{angle}}$) of the SAFT-$\gamma$ CG force field for $n$-$C_6H_{14}$, $n$-$C_9H_{20}$, and $n$-$C_{12}H_{26}$. The TraPPE-UA force field is used as the reference model in the atomistic MD simulations and equation (8) is used to determine the intra-molecular parameters. The results of the parametrization of the intra-molecular parameters at each state are reported together with the overall unweighed average values of each parameter.

| Compound  | $\rho$/(kg/m$^3$) | $T$/K | $r_0$/Å | ($k_{\text{bond}}$/$k_B$)/(K/A$^2$) | $\theta_0$/(deg) | ($k_{\text{angle}}$/$k_B$)/(K/rad$^2$) |
|-----------|-----------------|------|---------|--------------------------------|-----------------|--------------------------------|
| $n$-$C_6H_{14}$ |                 |      |         |                                  |                 |                                      |
|           | 658             | 381  | 3.51    | 5590                          | -               | -                                      |
|           | 585             | 432  | 3.49    | 6183                          | -               | -                                      |
|           | 233             | 609  | 3.45    | 7945                          | -               | -                                      |
|           | 23              | 432  | 3.50    | 6183                          | -               | -                                      |
|           | 8               | 381  | 3.52    | 5477                          | -               | -                                      |
| $n$-$C_9H_{20}$ |                 |      |         |                                  |                 |                                      |
|           | 676             | 446  | 3.50    | 6315                          | 163             | 1970                                   |
|           | 601             | 505  | 3.48    | 6939                          | 161             | 2199                                   |
|           | 232             | 713  | 3.44    | 8796                          | 158             | 2813                                   |
|           | 19              | 505  | 3.48    | 6893                          | 159             | 2161                                   |
|           | 6               | 446  | 3.50    | 6269                          | 160             | 1916                                   |
| $n$-$C_{12}H_{26}$ |                |      |         |                                  |                 |                                      |
|           | 678             | 494  | 3.49    | 6780                          | 160             | 2246                                   |
|           | 599             | 559  | 3.47    | 7396                          | 160             | 2405                                   |
|           | 227             | 790  | 3.44    | 9422                          | 156             | 3012                                   |
|           | 16              | 559  | 3.47    | 7404                          | 157             | 2352                                   |
|           | 4               | 494  | 3.50    | 6891                          | 159             | 2122                                   |
| Unweighed averages |           |      |         | 3.48                          | 6666            | 159                                    | 2318 |
Figure 2: Representative intra-molecular probability distributions for the stretching bonds and bending angles obtained for \( n\)-C\(_{12}\)H\(_{26}\) at two thermodynamic states (one supercritical, and one subcritical). The description is obtained using the reference TraPPE-UA force field with a 3:1 level of CG mapping. The symbols represent the results obtained from \( NVT \) molecular-dynamics simulations, and the continuous curves to the corresponding fits using Eq. 8 with a weighting factor of \( w(r) = 1 \) for the bond distributions and \( w(\theta) = \sin(\theta) \) for the angular distributions, respectively.
and supercritical states for each system are used for the parameterization. The subcritical states presented in Table 3 correspond to temperatures 15% and 25% below the critical temperatures of each n-alkane with corresponding densities that are 15% higher (lower) than the experimental saturated-liquid (vapour) densities to ensure single-phase states are considered. The supercritical states correspond to temperatures 20% above the reported experimental critical temperature for densities corresponding to the critical density.

The intra-molecular potentials are determined by defining effective CG beads, using the 3:1 mapping scheme described earlier, with the centre of mass (COM) calculated using the positions of the UA sites. The UA trajectories are used to compute the probability distribution of the effective bond distances and angles between the CG beads. Representative examples of distribution of bonds and angles for n-C\textsubscript{12}H\textsubscript{26} obtained from the NVT molecular-dynamics simulations are shown in Figure 2. In the calculations of the probability distributions no distinction between middle and terminal beads is made. A harmonic potential is employed to determine the average probability distributions for the bonds and angles of n-C\textsubscript{6}H\textsubscript{14}, n-C\textsubscript{9}H\textsubscript{20}, and n-C\textsubscript{12}H\textsubscript{26} for the thermodynamics states reported in Table 3 using weighted Gaussian distributions $P(x)$ of the form:

$$P(x) = \frac{w(x)}{\sqrt{2\pi s^2}} e^{-(x-\mu)^2/2s^2},$$

where $x$ is either the distance $x = r$ between adjacent beads or the the angle $x = \theta$ subtended by three consecutive beads, and the mean $\mu$ is $\mu = r_0$ or $\mu = \theta_0$, with $s^2$ the standard deviation. A weighting function $w(x)$ is used in Eq. 8 to take into account the asymmetry of the distributions, with $w(r) = 1$ for the bond distributions and $w(\theta) = \sin(\theta)$ for the angular distributions, respectively. The spring constants in Eq. 7 are then obtained as $k_{\text{bond}} \propto k_B T \ln P(r)$ and $k_{\text{angle}} \propto k_B T \ln P(\theta)/\sin(\theta)$, respectively\textsuperscript{76}.

The bond stretching and bending parameters of the SAFT-\(\gamma\) Mie CG force-field obtained from the UA trajectories are collected in Table 3 together with corresponding unweighed averages. For comparison, the bond constants reported by Shinoda et al.\textsuperscript{76} are of the order
of $k_{\text{bond}}/k_B = 6199 \text{ K/Å}^2$ and $k_{\text{angle}}/k_B = 1197 \text{ K/rad}^2$ ($\theta_0 = 173^\circ$ for angles involving middle-carbon beads); these values correspond to chains with more open angles and which are less rigid than those we determine in our CG mapping. In addition to the different choice of thermodynamic states used for the determination of these parameters, the differences can be also be attributed to the choice of the force field used in the fully atomistic simulations. Shinoda \emph{et al.} used an AA version of the CHARMM force field which explicitly takes into account the hydrogens in the $n$-alkane model, while here we consider the TraPPE-UA force field, which does not explicitly incorporate hydrogen atoms. It is likely that the charges incorporated on the hydrogen atoms of the CHARMM-AA force field result in distributions with more open angles.

The overall averages of the bonding constants over the thermodynamic states given in Table 3 are used to represent the bonded potential of the SAFT-\(\gamma\) Mie CG force field for \(n\)-alkanes. As the intra-molecular potential is obtained over a broad range of thermodynamic conditions, one would expect to have a better transferability (and representability) of the properties of \(n\)-alkanes. It is important to note that the value of $r_0$ obtained in the parametrization of the bond-length distributions is not used in the representation of the CG model. As we are using a tangent chain model within the SAFT-\(\gamma\) Mie description the corresponding bead diameters (cf. Table 1) are used instead.

### 2.3 SAFT-\(\gamma\) Mie CG force field for \(n\)-alkanes

The underlying model and assumptions of the SAFT-\(\gamma\) Mie EoS, in which third and higher body correlations are neglected, result in a force field in which the beads are connected tangentially by rigid bonds, with molecules best represented as fully flexible chains (bending or torsional potentials are not included), as proposed in earlier SAFT-\(\gamma\) Mie CG models\textsuperscript{47}. Bond stretching, bending, and torsional potentials are however usually included in simulations of molecular systems\textsuperscript{23,29,33,34} and are known to be important in the determination of the properties of dense systems, particularly the structure. The impact of the inclusion
of these intra-molecular interactions in our proposed force field is, therefore, of particular interest. With this in mind three SAFT-\(\gamma\) CG models (A, B, and C) are considered (cf. Table 4) to study a number of properties of \(n\)-alkane fluids with effective bond and bending constants for each of these models.

**Table 4: Summary of the effective bond and bending parameters used in our SAFT-\(\gamma\) CG force field models for \(n\)-alkanes.** Models A, B, and C are described in terms of effective bond \(k_{\text{bond,eff}}\) and bending \(k_{\text{angle,eff}}\) constants taken as multiples of the unweighed average values reported in Table 3. The equilibrium bond length \(r_0\) for all the models are taken from the diameters of the CG beads reported in Table 1.

| Model | \(r_0\) | \(k_{\text{bond,eff}}\) | \(\theta_0/(\text{deg})\) | \(k_{\text{angle,eff}}\) |
|-------|---------|-----------------|-----------------|-----------------|
| A     | \(\sigma_{kl}\) | 15 \(k_{\text{bond}}\) | 159             | 0               |
| B     | \(\sigma_{kl}\) | 15 \(k_{\text{bond}}\) | 159             | \(k_{\text{angle}}\) |
| C     | \(\sigma_{kl}\) | \(k_{\text{bond}}\)    | 159             | \(k_{\text{angle}}\) |

Model A \((k_{\text{bond,eff}} = 15 k_{\text{bond}}, k_{\text{angle,eff}} = 0)\) corresponds to a fully flexible model (no bending angle restriction) of tangentially bonded beads with essentially rigid bonds, i.e., the system represents a freely-jointed chain. This model is representative of the underlying model in the Wertheim TPT1 description at the heart of the SAFT-\(\gamma\) Mie EoS, on which the parametrisation of the inter-molecular potential is based. The bond constant is set to mimic a rigid bond (tangent spheres) with the aid of a large value which is 15 times larger than that obtained in the parametrization based on the TraPPE-UA simulations. In the case of model B \((k_{\text{bond,eff}} = 15 k_{\text{bond}}, k_{\text{angle,eff}} = k_{\text{angle}})\), the bonds are also considered rigid (with a large value of the bond constant) but a bending potential is incorporated, i.e., the model represents a semiflexible chain of tangent beads with rigid bonds. Model C \((k_{\text{bond,eff}} = k_{\text{bond}}, k_{\text{angle,eff}} = k_{\text{angle}})\) corresponds to the unmodified bonded potential parametrized with the aid of the TraPPE-UA force field presented in Table 3.
3 Theoretical Methods

We have used various efficient open-source software tools such as DL_POLY\textsuperscript{77}, GROMACS\textsuperscript{78}, LAMMPS\textsuperscript{79}, and HOOMMD-blue\textsuperscript{80,81} to carry out the simulations presented here. We have checked that the results are, as expected, independent of the software. The choice of software was made on the basis of exploiting the different techniques implemented in each of the codes.

Molecular dynamics (MD) simulations were carried out in the $NVT$ and $NPT$ ensembles with periodic boundary conditions using a time-step of 3 fs for the simulations using the TraPPE-UA force field and a time-step of 5 fs for the CG simulations. The cut-off for the intra-molecular interactions is fixed at 15 Å for the TraPPE-UA simulations and 30 Å for the CG simulations. This relatively long cut-off in the CG simulation is used to allow for comparison to the SAFT-$\gamma$ Mie theory; a shorter cut-off (24 Å) renders similar results. The temperature and pressure are controlled using a Nosé-Hoover thermostat and a barostat, respectively\textsuperscript{82,83}.

3.1 Thermodynamic properties

The vapour-liquid equilibrium properties of $n$-alkanes are determined using a direct coexistence method using MD-$NVT$ simulations. The molecules are arranged in an orthorhombic box with a constant volume $V = L_x \times L_y \times L_z$, such that $L_x = L_y << L_z$. After equilibration the density profile along the $z$ direction (normal to the interface) is used to determine the saturated densities of the vapour and liquid phases\textsuperscript{84}. The vapour pressures are calculated in two ways: in the first method the saturated gas density from the direct coexistence simulations is used to obtain the vapour pressure via the ideal gas law; in the second method, a single phase MD-$NVT$ simulation using the saturated gas density is carried out and the pressure is obtained through the virial route\textsuperscript{85,86}.

The vapour-liquid interfacial tension $\gamma$ is obtained from the diagonal components of the
pressure tensor\textsuperscript{87,88} as
\[
\gamma = \frac{L_z}{2} \left( P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right),
\]  
(9)
where \(P_{zz}\), \(P_{yy}\) and \(P_{xx}\) are the average values of the components of the main diagonal of the pressure tensor. The pre-factor 1/2 denotes the presence of two interfaces.

In the calculations using the TraPPE-UA force field, 7200 beads are used, while in the CG simulations 13800 beads are used, except for the simulations of \(n\)-C\textsubscript{60}H\textsubscript{122} and polyethylene where 11500 and 9000 CG beads are used, respectively, in simulations spanning up to 25 ns to allow relaxation of these long molecules. The simulations of these large molecular systems were carried out using the HOOMD-blue CUDA-enabled MD package to accelerate the calculations.

### 3.2 Transport properties

The diffusion coefficient \(D\) for \(n\)-alkanes ranging from \(n\)-C\textsubscript{6}H\textsubscript{14} to \(n\)-C\textsubscript{18}H\textsubscript{38} are obtained via calculations of the mean square displacement carrying out MD-NVT simulations using the Einstein relation:\textsuperscript{85,86} 
\[
D = \frac{\langle [r(t) - r(0)]^2 \rangle}{6t},
\]  
(10)
where \(r(t)\) is the position of the particle at time \(t\) and \(r(0)\) the reference position.

The viscosity is obtained using non-equilibrium MD (NEMD) simulations in the \(NVT\) ensemble with “sliding wall” boundary conditions\textsuperscript{89}. Simulation times of 30 ns with a time-step of 5 fs are performed. In order to determine the density in each case, MD-\(NPT\) simulations at \(T = 303\) K and \(P = 1\) MPa for \(n\)-C\textsubscript{12}H\textsubscript{26} and \(P = 0.1\) MPa for \(n\)-C\textsubscript{24}H\textsubscript{50} are run for up to 10 ns for equilibration of the density. Using the periodic perturbation method, the range of shear rates applied is 0.001, 0.002, 0.003, 0.004, 0.006, 0.008 and 0.01 nm/ps\textsuperscript{2}. Larger shear rates were also applied to ensure that the system was not in the shear thickening regime. These shear rates gave a linear regime for the equilibrium viscosity to be calculated by extrapolating to a zero shear rate. These simulations were carried out using GROMACS,
version 4.5.5. The viscosities of selected states for \( n-C_{12}H_{26} \) were also obtained using the reverse non-equilibrium molecular dynamics method of Müller-Plathe as implemented in LAMMPS using 10, 50, 100, and 200 momentum exchanges between layers.

4 Results and Discussion

In this Section the impact of including intra-molecular interactions on a number of structural, thermodynamic and transport properties for several \( n \)-alkanes is examined in detail by carrying out molecular dynamics (MD) simulations using the three SAFT-\( \gamma \) CG models presented in the previous section. The results of the simulations with the CG models are compared with the corresponding data with TraPPE-UA force field, with the results obtained using directly with the SAFT-\( \gamma \) Mie EoS where appropriate, and with available experimental data. All the details of the methodology for the simulations presented in this section can be found in section 3.

4.1 Structural properties of \( n \)-alkanes

The centre-of-mass pair distribution functions \( g(r) \) of \( n \)-hexane, \( n \)-nonane, and \( n \)-dodecane obtained from \( NVT \) molecular dynamics simulations using SAFT-\( \gamma \) Mie CG force fields A, B, and C for selected thermodynamic states used during the parametrization of the models, are presented in Figure 3. The results are compared with the results obtained from simulations using the TraPPE-UA force field.

We start by analysing the results for \( n \)-hexane. In our 3:1 CG model, \( n \)-hexane is treated as a dimer with two tangentially bonded terminal (T) beads, thus only models A and C are compared with the UA model. In terms of the contributions to the intra-molecular potential contributions, only bond stretching is considered; the difference between the results for models A and C for \( n \)-hexane is, therefore, only the stiffness of the bond potential. The pair distribution functions obtained for \( n \)-hexane are shown in Figure 3(a). It is apparent that
Figure 3: Centre-of-mass pair distribution function $g(r)$ obtained from simulations with TraPPE-UA$^{34}$ and SAFT-$\gamma$ Mie CG models A, B, and C for (a) $n$-hexane, (b) $n$-nonane, and (c) $n$-dodecane. The thermodynamic states are defined in each panel, correspond to states described in Table 3.
the simulation results for models A and C are essentially indistinguishable, suggesting that a bond constant \( k_{\text{bond}}/k_B = 6666 \text{ K/Å}^2 \) is large enough to keep the beads in our CG model tangential essentially corresponding to a rigid bond. For the lowest temperature \( (T = 381 \text{ K}) \), both CG models exhibit two maxima (at 6.5 Å and 11.0 Å) close to those characterizing the TraPPE-UA force field. The peak at \( \sim 6.5 \text{ Å} \) in the CG model is shaper compared to the UA model, due to the development of an additional peak at \( \sim 4.9 \text{ Å} \) that corresponds to the contact distance between two CG beads. This additional peak disappears as the temperature is increased; for \( T = 432 \text{ K} \), the peak at \( \sim 6.5 \text{ Å} \) in both CG models is almost as broad as in the case of the UA model. In the of the supercritical state at \( T = 609 \text{ K} \), the pair correlation functions for both CG models and the UA are essentially indistinguishable.

The pair correlation functions for \( n \)-nonane and \( n \)-dodecane are shown in Figures 3(b,c). At subcritical conditions \( (T = 446 \text{ K} \) and \( T = 505 \text{ K}) \), the curves obtained for \( n \)-nonane with the TraPPE-UA force field exhibit two shallow peaks located at \( \sim 5.8 \text{ Å} \) and \( \sim 8.8 \text{ Å} \). Both of the SAFT-\( \gamma \) CG models B and C, which take into account the bending contribution to the intra-molecular potential, exhibit the same features as the UA force field although sharper peaks are seen for the CG models. Model A, however, exhibits a single peak (located at \( \sim 7 \text{ Å} \)), confirming that a fully flexible model, corresponding to the underlying TPT1 representation\(^{66-71} \) inherent in SAFT approaches, does not reproduce the features that emerge from bending intra-molecular interactions. As in the case of \( n \)-hexane, the features observed with models B, C, and the UA model, merge into a single peak (located at \( \sim 8.0 \text{ Å} \)) for supercritical temperatures. A similar behaviour is observed in the case of \( n \)-dodecane, in which simulations with model A do not reproduce the features seen in the pair distribution functions obtained with the TraPPE-UA force field. The centre-of-mass radial distribution functions determined with models B and C reproduce reasonably well those of the UA model, again demonstrating the impact of including a bending potential in reproducing the structure of the fluids.
4.2 Vapour-liquid equilibria of \( n \)-dodecane

The SAFT-\( \gamma \) Mie CG model for \( n \)-dodecane comprises four beads: two terminal (T) beads and two middle (M) beads, providing a suitable case of study to assess the influence the intra-molecular interactions in the description of the vapour-liquid equilibria. The saturated densities of the liquid (\( \rho_l \)) and vapour (\( \rho_v \)) phases, the vapour pressures \( P_v \), and the vapour-liquid interfacial tensions \( \gamma \) are assessed in Figures 4(a-c). Molecular dynamics simulations are carried using the three SAFT-\( \gamma \) Mie CG models (A, B, and C) presented earlier, and the results are compared to corresponding data obtained from simulations with the TraPPE-UA force field, the SAFT-\( \gamma \) Mie EoS, and with the experimental data\(^72\). Overall, the three CG models provide a very good description of the experimental data, the TraPPE-UA data, and SAFT-\( \gamma \) Mie EoS. The calculated \%AADs with respect to the experimental data for each of the models are presented in Table 5.

In the case of the saturated liquid density \( \rho_l \), small differences are observed for the three CG models, the results of the UA model, and the experimental data. As expected these differences are more evident near the critical point. It is encouraging to note that the order of magnitude of the error is comparable for all of the models, including the more detailed UA model, with the advantage of an increase in the speed of the calculations in the case of the CG models due to the reduction in the number of beads used to represent the molecule. Very good agreement is apparent Figure 4 between the simulated results with the CG models and the predictions using the SAFT-\( \gamma \) Mie EoS, confirming the reliability of the theory employed to derive the molecular parameters.

In the case of the vapour pressure, the models considered provide a good description over the entire range of temperatures (from the triple point to the critical point). From a detailed examination of the calculated errors, we note that this is a very sensitive property to calculate via molecular simulation, while the \%AAD obtained is very small for the calculations carried out with the SAFT-\( \gamma \) Mie EoS (cf. Table 2); the molecular dynamics simulations lead to deviations which are an order of magnitude larger. The larger deviations occur at low
temperatures due to the low values of the vapour pressure of the longer \( n \)-alkanes, where
the simulation technique used for the calculation of \( P_v \) is not very accurate (cf. section
3.1). The deviations presented in Table 5 are given in absolute rather than relative terms
for a more appropriate comparison. In the case of the SAFT-\( \gamma \) Mie CG models, the smallest
deviations are found for Models B and C, with a slightly larger error apparent for model
A (in which a fully flexible CG chain model is used). All of the models considered provide
a good description of the vapour-liquid interfacial tension tension (cf. Figure 4 (c)) over
the entire temperature range, with small \%AAD found in each case. It is encouraging to
find that the proposed SAFT-\( \gamma \) Mie CG force field provide good description of the surface
tension, with \%AAD comparable to that obtained with the TraPPE-UA model; this is an
encouraging in terms of the representability of the CG models.

Overall, it is difficult to distinguish between the adequacy of the three SAFT-\( \gamma \) CG models
in the reproduction of the fluid-phase coexistence and interfacial tension of \( n \)-dodecane.
However, the comparisons provided in Figure 3 clearly highlight the advantage of using
a model with angle constraints (CG models B and C) in terms capturing the structural
properties of \( n \)-alkane fluids. In the calculation of bulk and interfacial tension properties
little difference is found between model B and C; a more accurate saturated liquid density
and pressure are obtained with model C, but a more accurate interfacial tension is obtained
with model B (cf. Table 5). The only difference between these two force fields is in the bond
constant, which in the case of model B corresponds to a effectively rigid bond. As a more
physical representation of a molecule corresponds to a harmonic bond rather than to a rigid
one, model C is adopted at this point to study the transferability of SAFT-\( \gamma \) Mie CG force
field for the description of the fluid-phase equilibria of other \( n \)-alkanes. We do not carry
out further calculations with model B, as similar values are expected. In a later section, we
resume the comparison of models A, B and C in examining transport properties to evaluate
the impact of the different terms in the bonded potential.
Figure 4: (a) Temperature-density vapour-liquid coexistence; (b) vapour pressures in both the standard and Clausius-Clapeyron representations; and (c) vapour-liquid interfacial tensions of $n$-dodecane. The continuous curves correspond to smoothed experimental data\textsuperscript{72}, the dashed curves (figures (a) and (b) only) to the description with the SAFT-$\gamma$ Mie EoS\textsuperscript{49}, and the symbols to data obtained from molecular simulations. The blue stars correspond to simulated values with the TraPPE-UA model, the red circles to the SAFT-$\gamma$ Mie CG model A, the blue triangles to model B, and the green diamonds to model C.
Table 5: Percentage absolute average deviation %AAD obtained with the SAFT-\(\gamma\) Mie EoS, with molecular dynamics simulations using the SAFT-\(\gamma\) Mie CG models A, B, and C, and with simulations using the TraPPE-UA for the saturated liquid density \(\rho_l\), and vapour-liquid interfacial tension \(\gamma\), and absolute deviations for the vapour pressure \(P_v\) for \(n\)-dodecane and \(n\)-hexacontane. The experimental data are from references\(^72,91\). The deviations in pressure are calculated as simple averages from \(\text{Dev} = \frac{1}{N_{\exp}} \sum_{i=1}^{N_{\exp}} |X_i^{\exp} - X_i^{\text{cal}}|\) as the values for this property are very small for the systems of interest.

| Model          | %AAD \(\rho_l\) | %AAD \(P_v/\text{MPa}\) | %AAD \(\gamma\) | %AAD \(\rho_l\) | %AAD \(P_v/\text{MPa}\) | %AAD \(\gamma\) |
|----------------|-----------------|------------------------|-----------------|-----------------|------------------------|-----------------|
| SAFT-\(\gamma\) Mie EoS | 1.05            | 0.003                  | -               | 14.11           | 0.019                  | -               |
| A              | 3.10            | 0.109                  | 8.09            | -               | -                      | -               |
| B              | 2.80            | 0.073                  | 5.34            | -               | -                      | -               |
| C              | 2.56            | 0.062                  | 9.00            | 13.93           | 0.041                  | 21.42           |
| TraPPE-UA      | 1.10            | 0.024                  | 7.67            | 7.99            | 0.005                  | 4.33            |

4.3 Transferability of the SAFT-\(\gamma\) Mie CG force field for \(n\)-alkanes

Following from the previous section, we proceed to test the transferability of the SAFT-\(\gamma\) Mie CG model C to describe the fluid-phase equilibrium properties of a range of \(n\)-alkanes from \(C_6H_{14}\) to \(C_{18}H_{38}\) as a function of temperature. The results of our molecular dynamics simulations are shown in Figures 5, compared with available the experimental data\(^72,73\) and with the theoretical description obtained using the SAFT-\(\gamma\) Mie EoS\(^49\). It is important to stress that the simulation results for \(n-C_6H_{14}\) and \(n-C_{18}H_{38}\) in particular are predictive for all properties, as no experimental data of these two alkanes were included in the parameterization of the force field. (We note, however, that atomistic simulations of the TraPPE-UA model for \(n-C_6H_{14}\) are used for the determination of the intra-molecular parameters in our force field). The vapour-liquid interfacial tension \(\gamma\) is predicted for all of the \(n\)-alkanes as this property is not used in the parametrization of the model.

The simulation results are found to be in good agreement with both the calculations with the SAFT-\(\gamma\) Mie EoS and with the experimental data for coexistence densities and vapour pressures as seen in Figure 5(a,b). The results obtained for \(\gamma\) using the SAFT-\(\gamma\) Mie CG model C are shown in Figure 5(c). Good agreement is seen in the case of the
longer \( n \)-alkanes, even at low temperatures, though we note that the predictions for \( n-C_6H_{14} \) exhibit slightly larger deviations for the interfacial tension at all temperatures. This larger deviation is justified given that only data for the longer \( n \)-alkanes, which contain terminal and middle beads, are used in the determination of the model parameters. In other work\(^7\) the terminal-terminal non-bonded bead-bead interactions are determined using target data for \( n \)-hexane, with the other parameters (those involving the middle-middle and the terminal-middle interactions) determined using longer \( n \)-alkanes.

Overall we find the agreement between the molecular dynamics simulations carried out with our SAFT-\( \gamma \) MIE CG force field (model C) to be very satisfactory when compared with experiment, from which we conclude that that the proposed SAFT-\( \gamma \) CG force field can be successfully applied to a range of \( n \)-alkanes, over a wide range of temperatures, pressures, and densities. The transferability of our force field is assessed for longer \( n \)-alkanes in the following section.

### 4.4 Predictions with SAFT-\( \gamma \) Mie CG force field for long-chain \( n \)-alkanes

#### 4.4.1 \( n \)-Hexacontane

We carry out molecular dynamics simulations for \( n-C_{60}H_{122} \) using our SAFT-\( \gamma \) Mie CG model C. The results for the fluid-phase coexistence properties and the vapour-liquid interfacial tension as a function of temperature are presented in Figure 6, with appropriate comparisons to correlated pseudoexperimental data from the DECHEMA database\(^9\). Also included in the comparison are simulation results using the TraPPE-UA force field\(^9\), and the theoretical predictions obtained using SAFT-\( \gamma \) Mie EoS\(^4\) with the same non-bonded parameters. As can be seen from the figure the agreement between the simulation data obtained with the SAFT-\( \gamma \) Mie CG model C and the experimental data is satisfactory for the properties considered. This is very gratifying considering that the model was developed for much shorter linear
Figure 5: (a) Temperature-density vapour-liquid coexistence; (b) vapour pressures in the Clausius-Clapeyron representation; and (c) vapour-liquid interfacial tensions of n-C$_6$H$_{14}$ to n-C$_{18}$H$_{38}$ obtained via molecular dynamics simulations using the SAFT-$\gamma$ Mie CG model C. The continuous curves correspond to the smoothed experimental data$^{72}$, the dashed curves (figures (a) and (b) only) to the description with the SAFT-$\gamma$ Mie EoS$^{49}$ calculations, and the symbols to the molecular-dynamics simulations of the CG model.
$n$-alkanes, and it further confirms the transferability of the proposed force field. A summary of the %AAD and deviations using the different models are reported in Table 5. Care should be taken, however, in interpreting these results, as $n$-alkanes are expected to be thermally unstable at temperatures above 650 K and the reported DECHEMA data\textsuperscript{91} are extrapolated correlations.

The coexistence envelope obtained from the CG simulations and the theoretical calculations are very close, and both are seen to slightly underpredict (more so at the higher temperatures) the experimental saturated liquid density. The data reported with the TraPPE-UA force field is also seen to underpredict the experimental saturated liquid density as observed in Figure 6(a), although to a lesser extent. One can also see from Figure 6 (b) that the SAFT-$\gamma$ Mie EoS calculations underpredict the vapour pressure over the temperature range considered. The enthalpy of vaporization (which is related to the slope of the curve) is however quite well represented; the proposed CG force field leads to a slightly larger slope of the Clausius-Clapeyron ($\ln P$ vs $1/T$) curve, overpredicting the pressure at high temperature and underpredicting it at low temperatures. The TraPPE-UA force field provides the best agreement at high temperature although it markedly overpredicts the vapour pressure at low temperatures.

As for the shorter $n$-alkanes considered earlier, we note that the vapour pressure is a notably difficult property to calculate accurately from molecular simulations in the case of very non-volatile substances; because the vapour pressure is very low, very few molecules are present in the vapour phase, which leads to poor statistics. We conclude that the overall agreement for all of the models considered is fair. The interfacial tension (Figure 6(c)) obtained with the SAFT-$\gamma$ Mie CG force field is in satisfactory agreement with experiment, although larger deviations are found at lower temperatures than with the TraPPE-AU model, which is very accurate for this property.
Figure 6: (a) Temperature-density vapour-liquid coexistence; (b) vapour pressures in the Clausius-Clapeyron representation; and (c) vapour-liquid interfacial tensions of for \( n \)-hexacontane \((n\text{-C}_{60}\text{H}_{122})\) obtained from molecular-dynamics simulations using the SAFT-\(\gamma\) Mie CG model C. The continuous curves correspond to smoothed experimental data from \(^{91}\), the dashed curves (figures (a) and (b) only) to the prediction with SAFT-\(\gamma\) Mie EoS, the blue stars to simulation obtained with the TraPPE-UA force field \(^{92}\), and the green diamonds to molecular-dynamics simulation with the CG model.
4.4.2 Polyethylene

The benefits and importance of developing accurate CG models for polymers has been highlighted in a recent paper\cite{93}. The typical molecular weight (degree of polymerisation) of a polymer is of the order of $10^5$ g/mol and the relaxation time scales of such systems are long, usually exceeding the duration of typical molecular simulation runs. In the case of polyethylene at least, molecular-weight dependence of the macroscopic properties tend to converge just beyond an entanglement length of 80 to 120 carbon atoms\cite{94,95}. This allows one to employ model systems with molecular weights of the order of 100 g/mol to provide reasonable comparisons with real polyethylene\cite{96}.

Here we carry out $NPT$ molecular-dynamics simulations of polyethylene systems containing 30 molecules each comprising 300 CG beads (i.e., corresponding to 900 backbone carbons, and a molecular weight of 12,602 g/mol). The same SAFT-$\gamma$ Mie CG model C force field (with bonded and non-bonded interactions) as for the simulations of the shorter $n$-alkanes and $n$-hexacontane are employed in the simulations of polyethylene. The vapour pressure of such high molecular weight species is effectively negligible and is not computed.

The density obtained with the SAFT-$\gamma$ CG model C are compared with experimental data of high-density linear polyethylene (HLDPE)\cite{97,98} as well as with the predictions of the SAFT-$\gamma$ Mie EoS at three pressures over a range of temperatures (see Figure 7). The average error for the density obtained from the molecular-dynamics simulations with respect to the experimental data corresponds to an overprediction of the density of 3.8%, with individual values ranging from 2.5%, at the highest temperature and lowest pressure, to 4.6% at the lowest temperature. The SAFT-$\gamma$ Mie CG force-field developed for the shorter $n$-alkanes is therefore seen to be transferable to model long-chain polyethylene. It is also useful to mention the small the difference between the molecular-dynamics data obtained with the CG model and the calculations with SAFT-$\gamma$ Mie EoS calculations ($\%AAD = 0.8$), confirming the excellent performance of the analytical equation of state.
Figure 7: Liquid density as a function of the temperature for high-density linear polyethylene (HLDP) at pressures of 0, 40, and 80 MPa. The symbols correspond to the predictions obtained from NPT molecular-dynamics simulations using the SAFT-\(\gamma\) Mie CG force field (model C), the dashed curves to the calculations obtained with the SAFT-\(\gamma\) Mie EoS, and the continuous lines to the experimental data.

4.5 Prediction of the transport properties of \(n\)-alkanes with the SAFT-\(\gamma\) Mie CG force field

Our comparison of SAFT-\(\gamma\) Mie CG force fields (models A, B, and C) presented in section B (cf. Table 4) did not highlight significant differences in the resulting description of the fluid-phase behaviour and interfacial tensions of the \(n\)-alkanes considered, although it is apparent, and perhaps unsurprising, that the microscopic structure of the fluid is very sensitive to the intra-molecular interactions. Here, we further consider transport properties in order to assess the importance of the bonded interactions in the representability of the SAFT-\(\gamma\) Mie CG force field. The viscosity and diffusivity of \(n\)-C\(_{12}\)H\(_{26}\) and \(n\)-C\(_{24}\)H\(_{50}\) (chosen as representative molecules that are small enough for ease of computation, but long enough to study the impact of the bonded potential) with the expectation that these transport properties will be subject to the details of the intra-molecular parameters.

4.5.1 Viscosity

The three SAFT-\(\gamma\) Mie CG models (cf. Table 4) are used to calculate the viscosity of \(n\)-dodecane at \(T = 400\) K and \(P = 1\) MPa. The results of the molecular-dynamics simulations
are presented in Table 6. It is immediately apparent that the fully flexible model A leads to an underprediction (of 17.5%) of the experimental data, whereas models B and C, in which a bonded potential is considered, lead to values considerably closer to the experimental values (7.5% error for the case of model B and 2.5% with model C). This is encouraging considering the coarse-grain nature of the force field, and the fact that it was not parametrized for transport properties. It is, however, difficult to unequivocally assert which of models B and C is better in describing the viscosity of \( n \)-dodecane, keeping in mind that the experimental values are reported to carry an uncertainty of up to 5%, and that the two models differ only in the stiffness of the bond potential.

We have also carried out calculations using model C with an additional torsional (dihedral) contribution, using a similar procedure to used in Section 2.2. The value obtained for the torsional constant of the \( n \)-alkanes is found to be less than \( k_B T \). The incorporation of the torsional contribution is therefore found to have minimal impact the description of the viscosity of \( n \)-dodecane (data not shown). One should however acknowledge that the small effect observed in the case of \( n \)-dodecane, may be more important in longer \( n \)-alkane chains and polymers and should not be ruled out in further investigations. At this point, given the slightly better performance of SAFT-\( \gamma \) Mie CG models C for the prediction of viscosity, we continue to use model C to compute the viscosity over a range of temperatures for both \( n \)-dodecane and \( n \)-tetracosane.

Table 6: Viscosity \( \eta \) (at a temperature of 400 K and pressure of 1 MPa) and diffusion coefficient \( D \) (at a temperature of 303 K and a density of 0.00446 mol cm\(^{-3}\)) obtained for \( n \)-dodecane (\( n \)-C\(_{12}\)H\(_{26}\)) using the SAFT-\( \gamma \) CG models A, B, and C (cf. Table 4). The experimental values\(^{100,101}\) are included for comparison.

| Models | \( \eta/cP \) | \( D \times 10^5/(cm^2 s^{-1}) \) |
|--------|----------------|-----------------------------|
| A      | 0.33 ± 0.01    | 1.19 ± 0.01                 |
| B      | 0.43 ± 0.01    | 0.84 ± 0.01                 |
| C      | 0.39 ± 0.01    | 0.96 ± 0.01                 |
| Exp    | 0.40 ± 0.01\(^{72}\) | 0.89 ± 0.01\(^{100}\) |
|        |                 | 0.94 ± 0.03\(^{101}\)      |
The viscosities of \( n\text{-C}_{12}\text{H}_{26} \) and \( n\text{-C}_{24}\text{H}_{50} \) are plotted over a range of temperatures in Figure 8. The corresponding experimental and simulation data presented are collected in Table 7. Overall we find that the proposed coarse-grain force field provides an accurate prediction of this transport property, confirming the representability of the SAFT-\( \gamma \) Mie CG model C. As can be seen from the figure, the viscosity of \( n\text{-dodecane} \) is predicted accurately over the entire temperature range considered. Although in the case of \( n\text{-tetracosane} \) the viscosities obtained with the CG model underpredict the experimental values at lower temperatures (which could be an indication of the onset of solidification), with a slight overprediction of the data at higher temperatures, overall the representation can be considered adequate. The average absolute deviation from the experimental values is less than 5% for \( n\text{-dodecane} \) and 15% for \( n\text{-tetracosane} \). The activation energy for viscous flow can be calculated from the expression \( \eta = \eta_0 \exp(\frac{E}{RT}) \) using the temperature-dependence of the data. Excellent agreement with experiment is found for \( n\text{-C}_{12}\text{H}_{26} \), with values of \( \frac{E}{R} \)\text{sim} = 1670 K and \( \frac{E}{R} \)\text{exp} = 1721 K. In the case of \( n\text{-C}_{24}\text{H}_{50} \) a larger deviation is noted, mostly due to the under-prediction of the viscosity at the lowest temperature considered: an activation energy of \( \frac{E}{R} \)\text{sim} = 1640 K is obtained from the CG simulation data, while the experimental value is \( \frac{E}{R} \)\text{exp} = 2029 K.

The transport properties of \( n\)-alkanes using CG models based on fully-flexible chains of Lennard-Jones segments have been reported in a recent study by Galliero. Larger errors were obtained for the viscosity for lower temperatures with a flexible model, and Galliero notes that an additional parameter to take into account the ‘rigidity’ of the molecule is needed to improve the accuracy of the description. It is unfortunately difficult to make a direct comparison with our model as different chain lengths are considered; we note, however, that the use of the Mie potential (instead of a fixed-range 12-6 Lennard-Jones form) and the inclusion of intra-molecular interactions in our SAFT-\( \gamma \) Mie CG force-field provides a force-field that is transferable over thermodynamic states and that performs well in terms of representing a range of thermophysical properties, including the viscosity.
Figure 8: Viscosity $\eta$ for $n$-dodecane at 1 MPa and $n$-tetraocane at 0.1 MPa obtained from molecular-dynamics simulations with the SAFT-$\gamma$ Mie CG model C, compared to experimental data $^{72,102}$.

4.5.2 Diffusivity

The diffusion coefficient is an important transport property that can be easily calculated from molecular-dynamics simulations; the theoretical prediction of the diffusivity of dense fluids is still lacking $^{48}$. The diffusivity serves as a further test of the representability of the SAFT-$\gamma$ Mie CG force field. The diffusion coefficient for $n$-C$_{12}$H$_{26}$ is calculated first by carrying out NVT molecular-dynamics simulation at one state point ($T = 303$ K and $759.7$ kg m$^{-3}$) with the SAFT-$\gamma$ Mie CG models A, B, and C (cf. Table 4), in order to assess the impact of the different contributions in the bonded potential, by comparison to experimental data $^{103}$. The results are collected in Table 6 and shown in Figure 9. It is encouraging to find that our SAFT-$\gamma$ force fields provide a reasonable description of diffusion coefficient even though transport properties are not considered in the parametrization of the intra- and inter-molecular interactions.

In more detail, we note the larger deviation from the experiment for model A. As in the case of viscosity, it is difficult to differentiate between the performance of models B and C. In this case, this is due in part to the large uncertainty in experimental values $^{100,101}$. Overall the findings allow us to conclude once again that there is indeed an advantage of incorporating the intra-molecular potential in the SAFT-$\gamma$ CG force field in terms of the
Table 7: Density $\rho$ and viscosity $\eta$ of $n$-dodecane at 1 MPa and $n$-tetracosane at 0.1 MPa obtained from molecular-dynamics simulations with the SAFT-$\gamma$ Mie CG force field (FF) model C. The simulation results for the viscosity are compared to experimental data.$^{72,102}$

| $T$ /K | $\rho$ / (kg m$^{-3}$) | $\eta_{\text{exp}}$ / cP | $\eta_{\text{Model C}}$ / cP |
|---|---|---|---|
| $n$-C$_{12}$H$_{26}$ | | | |
| 350 | 720.5 | 0.65 | 0.65 ± 0.01 |
| 400 | 672.8 | 0.40 | 0.39 ± 0.01 |
| 450 | 632.0 | 0.26 | 0.28 ± 0.01 |
| 500 | 584.3 | 0.18 | 0.20 ± 0.01 |
| 550 | 524.6 | 0.12 | 0.13 ± 0.01 |
| 600 | 439.5 | 0.08 | 0.08 ± 0.002 |
| $n$-C$_{24}$H$_{50}$ | | | |
| 333 | 795.9 | 4.19 | 3.46 ± 0.01 |
| 372 | 765.4 | 2.08 | 2.00 ± 0.01 |
| 422 | 728.1 | 1.10 | 1.26 ± 0.01 |
| 477 | 680.7 | 0.65 | 0.77 ± 0.01 |
| 505 | 660.4 | 0.52 | 0.64 ± 0.01 |

computation of transport properties. Moreover, given that model C incorporates a more realistic representation of the bond constant as well as providing a slightly better prediction of the transport properties studied (especially noticeable for the viscosity), we proceed to use model C to predict the diffusivity of a number of $n$-alkanes as a further challenge to the transferability and representability of the CG force field.

Diffusion coefficients for $n$-C$_8$H$_{18}$ to $n$-C$_{16}$H$_{34}$ are determined from $NVT$ molecular-dynamics simulations at 303 K for the densities reported in Table 8 using the SAFT-$\gamma$ Mie CG force field Model C. The simulated values are compared to experimental data$^{103}$ and with the CG simulations reported by Nielsen et al.$^{33}$ in Figure 9. The experimental data presented here only spans a limited range of $n$-alkane chain lengths, but it suffices to reveal a trend with molecular weights at the selected temperature. As can be seen in the figure, we find good agreement between the simulation data obtained with the SAFT-$\gamma$ Mie CG model C and the experimental data available. We note the larger (negative) slope in the
Table 8: Diffusion coefficient $D$ calculated via $NVT$ molecular-dynamics simulations with the SAFT-$\gamma$ Mie CG force field, model C, for a number of $n$-alkanes at $T = 303$ K. The density $\rho$ used for each system is also given, corresponding to the resulting equilibrium density from $NPT$ simulations at a temperature of $T = 303$ K and pressure of $P = 1$ MPa.

| $n$-Alkane | $\rho$ / (kg m$^{-3}$) | $10^5 D_{\text{Model C}}$ / (cm$^2$ s$^{-1}$) |
|------------|------------------------|------------------------------------------|
| $n$-C$_6$H$_{14}$ | 661.8 | 3.37 ± 0.03 |
| $n$-C$_9$H$_{20}$ | 722.1 | 1.67 ± 0.01 |
| $n$-C$_{12}$H$_{26}$ | 759.7 | 0.96 ± 0.01 |
| $n$-C$_{15}$H$_{32}$ | 783.8 | 0.60 ± 0.01 |
| $n$-C$_{18}$H$_{38}$ | 801.7 | 0.41 ± 0.01 |

diffusion coefficient with chain length; the diffusion coefficients simulated with the SAFT-$\gamma$ Mie CG force field underpredict the experimental values for the shorter chains and slightly overpredict those for the longer chains, but overall the agreement can be considered very satisfactory. The simulated values obtained with the CG model of Nielsen et al. are seen to lead to an overprediction of the diffusion coefficient corresponding to much faster dynamics. They also a 3:1 CG level of mapping, but use Lennard-Jones interactions to describe the bead-bead interactions instead of the harder Mie form incorporated in our SAFT-$\gamma$ Mie CG force field. The choice of a more repulsive bead-bead interaction ($\lambda_{kl}^{r} \sim 16$) allows us to obtain a better prediction of the transport properties. It is important to emphasize that this value of the repulsive exponent is estimated from vapour-pressure and saturated-liquid density equilibrium data alone in the parametrization of the inter-molecular potential; the transport or interfacial properties are not used in the development of the model.

5 Conclusions

A SAFT-$\gamma$ Mie CG heteronuclear model for linear alkanes has been developed incorporating intra-molecular (bonded) and and inter-molecular (non-bonded) interactions with the aim of addressing the transferability, representability and robustness of the force field. We have
Figure 9: Diffusion coefficient $D$ for $n$-alkanes obtained by NVT molecular-dynamics simulations with the SAFT-$\gamma$ CG force field model C at a temperature of 303 K and the corresponding densities for a pressure of 1 MPa. The experimental data\textsuperscript{103} and simulation data for the CG model of Nielsen et al.\textsuperscript{33} parameterized using surface tension data are shown for comparison. Continuous curves have been added to aid the visualization of the slopes.

carried out molecular dynamics simulations of the structural (radial distribution function), thermodynamic (fluid-phase equilibria and interfacial tension), and transport (viscosity and diffusivity) properties for a number of $n$-alkanes, making appropriate comparisons with the available experimental data and the results of united-atom simulations.

In the force field three carbon atoms are incorporated in each CG bead (corresponding to a 3:1 level of resolution) differentiating the terminal (CH$_3$-CH$_2$-CH$_2$-) and and middle beads (-CH$_2$-CH$_2$-CH$_2$-). The inter-molecular interactions are represented with Mie (generalised Lennard-Jones) potentials. The relevant parameters are obtained using the SAFT-$\gamma$ Mie EoS\textsuperscript{49}, which is of sufficient accuracy to provides a direct link between the force-field parameters and the simulation of the macroscopic properties. The use of the algebraic EoS allows one to consider broad ranges of thermodynamic data in the parameterization of the model; here the vapour pressure and saturated-liquid densities over the entire fluid range are chosen as the target properties. The intra-molecular interactions incorporate bond and angle contributions, which are obtained following a bottom-up approach using Trappe-UA models; we find a very small effect for the dihedral contribution, which is hence neglected.

The resulting force-field provides a very accurate description of the coexistence properties
of the \( n \)-alkanes used in the parameterization (\( n \)-nonane, \( n \)-dodecane, and \( n \)-pentadecane) and is transferable in the prediction of the thermodynamic properties of \( n \)-alkanes not included in the parametrization, including long linear alkanes and polymers; in particular \( n \)-C\(_{60}\)H\(_{122}\) and a linear polyethylene of 900 carbons. The force field performs very well in terms in terms of representability. We report simulated values of the transport properties (viscosity and diffusivity) which are shown to be good agreement with experiment for a range of \( n \)-alkanes. The level of agreement we find in terms of the diffusivity is particularly encouraging.

A detailed assessment of the impact of the bonded potential in the SAFT-\( \gamma \) Mie CG force field is made by provided comparisons between three models: a pearl-necklace chain (fully flexible with rigid bonds), a semiflexible chain with rigid bonds, and a semiflexible chain with harmonic bonds. Interestingly, little difference between these three cases is found for the fluid-phase behaviour of \( n \)-dodecane. As expected, however, the inclusion of the intra-molecular bonded potential is critical in terms of reproducing the structural properties of the system. Furthermore, the fully flexible model is found to present larger deviations in the description of the transport properties simulated; a good prediction of the viscosity and diffusivity is achieved by incorporating the intra-molecular interactions.

In conclusion, a transferable CG force-field is presented for \( n \)-alkane fluids, which includes bonded and non-bonded interactions. The model can now serve as the bases to continue expanding the SAFT-\( \gamma \) Mie family of force fields by including other chemical groups of interest for more complex systems such as branched hydrocarbons, alcohols, surfactants, and multi-functional polymers.

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Figure 10: TOC