

# Discriminating between Correlations of Experimental Viscosity Data for Perfluorobutane Using Molecular Simulation

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As part of a long-term project aimed at examining the rheology of fluorinated compounds of industrial importance, we have in an initial study been examining the ability of different potential models to predict the viscosity of perfluoroalkanes. Here we present a comparison of the viscosity of perfluorobutane predicted by molecular dynamics simulations using two different potential models with two experimentally based correlations, one of which is used in the DIPPR database. We find that the simulation data enables us to discriminate between two sets of published correlations for the viscosity of perfluorobutane.

## Introduction

In recent years there has been considerable interest in fluorinated compounds. In particular, the unique combination of physical and chemical properties observed in the perfluorocarbons suggests their potential for many useful applications.<sup>1,2</sup> Given the structural similarity with the corresponding hydrocarbons, it is quite surprising that the perfluorocarbons actually display very different physical and chemical properties. For example, their densities and viscosities are higher, though surface tensions, refractive indices, and dielectric constants are lower. Furthermore, in addition to their chemical and physical stability, they are nonflammable and physiologically inert. This remarkable chemical and biochemical inertness has led to the perfluorocarbons attracting a lot of interest in biomedical applications; for example, the first commercial synthetic oxygen carriers or “blood substitutes” were, in fact, based on perfluorocarbons.<sup>2</sup> Additionally, fluorocarbons are important to a number of applications in the chemical industry, for example, as refrigerants,<sup>3</sup> as blowing agents such as Solvay Fluor’s Solkane, and as components of surfactant molecules in the solubilization of supercritical carbon dioxide.<sup>4,5</sup>

Recently, there has been interest in perfluoropolyalkyl ethers and their application as lubricants,<sup>6,7</sup> such as DuPont’s Krytox. With these systems in mind as our long-term target, we have been testing the ability of different potential models to predict the viscosity of perfluoroalkanes for which we have experimental or correlated data to compare with. In the literature there is limited experimental data available for the viscosity of perfluoroalkanes. For perfluorobutane, we have been able to locate two sources of pseudo experimental data. The first comes from the DIPPR database and is based

on a correlation by Van-Velzen and co-workers,<sup>8</sup> and the second is a correlation of experimental data published in 1990 as a report by the Oak Ridge Gaseous Diffusion Plant.<sup>9</sup> Upon inspection of the data, it is clear that the two sources are in significant disagreement with each other. Henceforth, we refer to these as the DIPPR and ORGDP correlations, respectively.

In this paper we present preliminary results for the viscosity of perfluorobutane from equilibrium (EMD) and nonequilibrium molecular dynamics (NEMD) simulations using two different potential models, the results of which enable us to discriminate between these two correlations for the viscosity of perfluorobutane.<sup>8,9</sup> We are unaware of any previous case in which simulation results for viscosity have been used to discriminate between experimental data or between correlations of experimental data. However, we are aware of cases in which simulation has been used to uncover inaccuracies in processing raw neutron scattering data<sup>10</sup> and one case in which simulation was used to discriminate between experimental data on the critical constants of the *n*-alkanes.<sup>11</sup>

## Models

While much work has been done on characterizing force fields for hydrocarbons, force-field development and simulation of perfluorocarbon systems is much less advanced. There have been relatively few studies published in the literature on perfluoroalkane systems (see, for example, refs 12–16) which have resulted in the development of a force field. By comparison, many alkane force fields have been proposed and tested in the literature. In this work we have chosen the united atom (UA) model developed by Cui et al.,<sup>17</sup> because at the time of publication it was shown over a range of state points to perform better than those used previously by other authors.<sup>17</sup> This force field was parametrized from calculations of vapor–liquid phase equilibria, and good agreement was obtained with experimental data for the critical temperatures, densities, and saturated liquid densities for a number of perfluoroalkanes. We note that this model was not designed to predict transport properties. In the UA model the CF<sub>2</sub> and CF<sub>3</sub> groups are represented as single Lennard-Jones interaction sites

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with the interaction center located at the center of the carbon atoms. Details of the bonded interactions can be found in the original paper<sup>17</sup> (model T), although we make the modification that the fixed bond length is replaced by a simple harmonic potential with a C–C force constant taken from the work of Holt and Farmer.<sup>18</sup>

In the second model developed by Smith and co-workers, in contrast to the UA model, both of the carbons and fluorines are explicitly taken into account. We will refer to this model as explicit atom (EA). The van der Waals parameters of nonbonded interactions were parametrized based on ab initio electronic structure calculations performed on a CF<sub>4</sub>–CF<sub>4</sub> dimer.<sup>19</sup> Valence parameters and the torsional potential were parametrized in order to reproduce high-level quantum chemistry calculations on short perfluoroalkanes (C<sub>4</sub>F<sub>10</sub>, C<sub>5</sub>F<sub>12</sub>, and C<sub>6</sub>F<sub>14</sub>).<sup>20</sup> We note that this is a preliminary version of the force field, which has been shown to adequately perform for short molecules at low temperatures (200 K < *T* < 400 K). Work is underway to improve the accuracy in determining the thermophysical and conformational properties of longer chains at higher temperatures (*T* > 400 K).

For a C<sub>*n*</sub>F<sub>2*n*+2</sub> perfluorocarbon, the explicit atom potential contains an additional 2*n* + 2 sites compared to the *n* sites used in the UA description. Therefore, the EA model requires substantially more computational time than the UA model for the same length of trajectory, with the trade-off being that the EA model should represent the potential energy surface between molecules more accurately than the UA representation. Our experience is that a UA model will underpredict the viscosity, unless it is specifically parametrized to reproduce experimental transport properties. Thus, it is not surprising that the UA model used here, being fitted to thermodynamic data, underpredicts the experimental viscosity. We interpret this underprediction as a consequence of the UA potential surface being smoother than the EA surface, resulting in easier sliding of one molecule over another and thus leading to a lower viscosity. Both of these potentials represent state of the art in UA and EA models, respectively, and are currently not available in any commercial simulation program.

## Results and Discussion

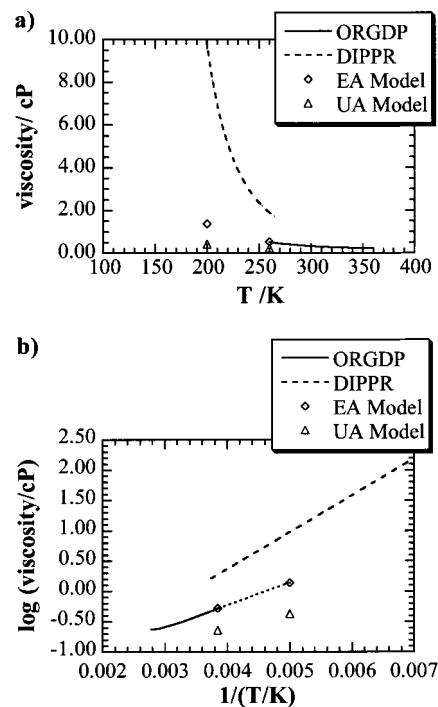
Using the UA model, the viscosity of perfluorobutane has been determined through NEMD simulation over a range of strain rates. The density for each state point at atmospheric pressure was obtained from the DIPPR database, giving at 200 K a value of 1.817 g cm<sup>-3</sup> and at 260 K a density of 1.636 g cm<sup>-3</sup>. At high shear rates, we observed the usual shear-thinning behavior, leading to a Newtonian plateau at the lower strain rates. The zero-shear viscosity was determined from the NEMD results by averaging the values that appeared to fall within this Newtonian plateau.

For the EA model, EMD simulations were performed and the shear viscosity was computed using an Einstein relation between the viscosity and fluctuations of the stress tensor (details of this procedure can be found elsewhere).<sup>21</sup> Constant pressure–constant temperature (*NPT*) simulations were performed at each temperature in order to establish the equilibrium densities at atmospheric pressure. Densities of 1.828 and 1.601 g cm<sup>-3</sup> at 200 and 260 K, respectively, were obtained (Table 1), which are in close agreement with

**Table 1. Viscosity Data for Perfluorobutane in CP at 200 and 260 K**

temp/K	density/(g cm <sup>-3</sup> )	UA	EA	DIPPR	ORGDP
200	1.817 <sup>a</sup>	0.43	1.40	9.58	1.46 <sup>c</sup>
260	1.636 <sup>b</sup>	0.23	0.53	1.91	0.52

<sup>a</sup> EMD performed at 1.828 g cm<sup>-3</sup>. <sup>b</sup> EMD performed at 1.601 g cm<sup>-3</sup>. <sup>c</sup> Extrapolated to 200 K. Correlation was developed for 260 K ≤ *T* ≤ 360 K.



**Figure 1.** (a) Comparison of the viscosity of perfluorobutane computed by NEMD and EMD simulations (symbols) and as determined by two published correlations (lines). (b) Comparison of the viscosity of perfluorobutane as a semilog plot of viscosity vs temperature. The symbols are the simulation results, the solid and dashed lines are the DIPPR and ORGDP correlations, respectively, and the dotted line is an extrapolation of the ORGDP correlation to 260 K.

the experimental values reported in the DIPPR database. The production runs were performed in a constant volume–constant temperature ensemble.

The results of both the NEMD and EMD simulations at each state point are presented in Figure 1. The error bars are omitted from the figures for clarity, because they are smaller than the symbols. First, we note from the table that the UA viscosity is less than the EA viscosity at these state conditions. This is in line with the expectations described in the previous section. Second, we see from the figure that both simulations agree with the ORGDP correlation at 200 and 260 K, and in the case of the EA model, the agreement is quantitative. To further illustrate this point, in Figure 1b the same plot is shown as log viscosity vs inverse temperature. From this we see the ORGDP correlation and the EMD simulation results fall on a straight line, suggesting that the EMD simulations are consistent with the ORGDP correlation over a wide temperature range. This suggests that the DIPPR correlation is in error by approximately an order of magnitude at the higher temperature. At the lower temperature, the ORGDP correlation is in qualitative agreement with the simulations (quantitative for the EA model) while the DIPPR correlation is evidently quite incorrect. On this basis we conclude that the DIPPR correlation is

incorrect. We are unsure how the DIPPR correlation was developed, as the original source is not available to us. The ORGDP correlation was based on extrapolation from experimental data on higher perfluoroalkanes. It is possible that less experimental data was available at the time when the DIPPR correlation was postulated.

## Conclusions

We have presented preliminary results from a study of the viscosity of perfluoroalkanes through molecular simulation. In this initial work results of molecular dynamics simulations for perfluorobutane at two state points are reported. The main focus of this paper is to highlight the clear inconsistency between the two sets of correlated data. It is obvious from the figure that the correlation cited in the DIPPR database is inconsistent with the simulation results. The simulation data obtained with the fully atomistic potential are in excellent agreement with the ORGDP correlation; although the UA model underpredicts the viscosity, it supports the same conclusion. Further evidence to support this conclusion is provided by examining the viscosity of the C<sub>5</sub>–C<sub>7</sub> perfluoroalkanes. The ORGDP correlation was based on the viscosity of higher perfluoroalkanes and so is fully consistent with the viscosity for C<sub>5</sub>–C<sub>7</sub>, while the DIPPR correlation is not. Additionally, preliminary simulations of the viscosity of perfluoropentane, perfluorohexane, and perfluoroheptane with both of the UA and EA models are consistent with the experimental data providing further evidence to support our conclusion. The fact that we are able on the basis of simulation to discriminate between these two correlations is evidence of the growing sophistication of molecular simulation methods and the increasing accuracy of force fields.

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