

Determination of Diesel Physical Properties at Injection Pressures and Temperatures via All-Atom Molecular Simulations

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ABSTRACT

Fuels are subjected to extreme conditions inside a fuel injector. In modern common rail diesel engines, fuel temperatures can reach 150°C and pressures can exceed 2500 bar inside the rail. Under such conditions the fluid physical properties of the fuel can differ substantially from ambient pressure and temperature and can impact the spray behavior and characteristics. Moreover, experimental determination of the fuel physical properties at these extreme conditions can be very difficult.

Previously it has been shown that for pure components, all atom molecular simulations offer a reliable means to calculate the key physical properties (including transport properties, e.g., viscosity) at FIE representative conditions. In this study we extend the approach to calculate these properties of binary mixtures using atomistic molecular simulations. We modelled the diesel fuel using two diesel surrogates: a modern "GTL-like" diesel fuel surrogate, n-hexadecane, and a "conventional" diesel fuel surrogate n-decylbenzene and calculated viscosity and density for the respective pure components and their various binary mixtures.

The molecular dynamics simulations provide insights into the mechanisms at an atomic level and can reliably calculate density and viscosity of the fuel at extreme conditions commonly found inside a fuel injector.

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INTRODUCTION

The rheological properties of hydrocarbons are of great interest for the petroleum and automobile industries. Optimization of such properties in fuels and lubricants through a judicious combination of compounds and additives has been a long-standing matter of research. One defining characteristic of such fluids is their shear viscosity. A uniform shear viscosity profile across the range of temperature and pressure is desired for a good lubricant and specific patterns of material behavior would be desired for fuels. Although the experimental determination of this quantity for pure fluids and for mixtures has been pursued, its prediction from inter-molecular interactions is sought. Experimental measurements at elevated temperatures and pressures can also incorporate potential uncertainties related to experimental setup and instrumentation. Under these conditions calculations via molecular simulations takes full account of interactions at an atomic level to calculate the properties of interest without involving the cost of samples and the hazards of extreme conditions under experiments. Thus these models enable us to study such properties under extreme conditions that are either not possible or hazardous for experimental investigation. These molecular methods will provide the ability to fine tune the composition for a product optimization as well as to potentially understand the influence of novel additives to fuels and lubricants.

Molecular simulation has long been used to gain understanding of phenomena observed in physical systems. In particular, macroscopic transport properties such as viscosity, diffusivity, thermal conductivity, etc., may be computed by using molecular simulation methods such as the molecular dynamics or Monte Carlo methods. There are two types of molecular dynamics approaches to these calculations: equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD). In the EMD approach, transport properties are obtained based on the unforced response of a collection of energy conserving molecules by using the so-called Green-Kubo relations. The basis of such approximation is the observation that the molecular response due to a weak external excitation decays in the same way as a spontaneous fluctuation at equilibrium.

Prediction of alkane viscosity at high pressures up to 2000 bar (typical in a common rail diesel engine condition) is a rather challenging problem. A critical review of the literature reveals that majority of the molecular simulation studies of alkane viscosity use various United Atom (UA) models which typically underestimate viscosity by 20% to 80% [1]. There are relatively fewer reports on simulation of transport properties using all-atom (AA) potentials [2] [3]. Allen and Rowley optimized the OPLS-AA force field interaction parameters for both short and long alkanes [2]. They observed an increasing positive deviation for viscosity of n-butane with increasing density. For n-nonane, Martin et al. observed 40% deviation from

experimental viscosity using the OPLS-AA force field [3]. In case of perfluoroalkanes, the OPLS-AA force field interaction parameters shows 15% to 35% deviation from experimental viscosity values [4].

Recently we have developed an EMD based approach using multiple independent trajectories with all-atom interaction potential to reproduce n-hexadecane (representative of GTL diesel fuel) and ndecylbenzene (representative of conventional diesel fuel) viscosity (up to 750 bar pressure and at 423 K temperature) within 12% and 8% accuracy respectively (unpublished data). For lubricant size molecules we found NEMD to be more effective in reproducing viscosity temperature relation (within 6% accuracy for C30 isomers) at ambient pressure as well as magnitude of viscosity even at high pressure up to 2000 bar (within 10% accuracy for C30 isomers) [5]

In this article we have extended our EMD protocol to study the viscosity profile of two binary mixtures as a function of pressure. One mixture involves two n-alkanes, n-octane (C_8H_{18} ; Figure 1a) and n-dodecane ($C_{12}H_{26}$; Figure 1b) (case 1) and the other involves two diesel surrogates, n-hexadecane and n-decylbenzene (case 2). n-hexadecane ($C_{16}H_{34}$) represents GTL (Gas to Liquid) like diesel and while n-decylbenzene ($C_{16}H_{26}$) represents regular aromatic diesel as shown in Figure 1c and 1d respectively.

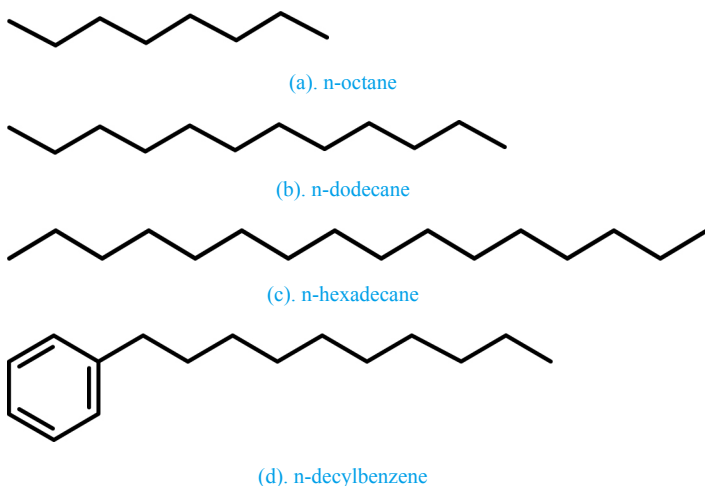


Figure 1. Chemical Structures of molecules studied in this report.

In case 1, we compare our simulation results with experimental data available from literature. In case 2, we compute the viscosities of various binary mixtures (20:80, 40:60, 60:40 and 80:20) of the two representative diesel surrogates (n-hexadecane and n-decylbenzene).

METHODS

In our previous work with n-hexadecane, we have used the Tu-Tobias-Klein force field [6] with which we were able to reproduce densities and viscosities within 1% and 10% relative errors vs. experimental values respectively [7]. The Tu-Tobias-Klein force field has been particularly developed for linear molecules and parameters are not available for other topologies e.g. cyclic aromatic/aliphatic molecules. For this reason, we have chosen to adopt a more generic force-field OPLS (Optimized Parameters for Liquid Simulations) [8] for our simulations. It is known from literature that OPLS all-atom

force field fails to reproduce viscosity results for long hydrocarbons in its native format. Alternative approaches have been reported [9,10] with changes in Lennard-Jones parameters, backbone dihedral (C-C-C-C) parameters and partial charges of C and H atoms to reproduce densities, heats of vaporization, self-diffusion and viscosities of long hydrocarbons. We have tested the parameters reported in some of the external publications to see their ability to accurately reproduce density/viscosity of n-hexadecane. Based on our study we found that the parameters developed by Sui *et. al* [10] (LOPLS) reproduced densities and the heats of vaporization of alkanes and alkenes of different lengths (both short and long hydrocarbons) and therefore were chosen for n-hexadecane. As the study was limited to alkanes and alkenes, no specific parameters or comments were reported for aromatic components. In case of n-decylbenzene, parameters for aromatic/ring carbons and the respective bonded hydrogen atoms are not reported by the Sui *et. al.*, we have used OPLS parameters. Further in this report, we continue to refer to this force field as LOPLS.

Our protocol includes two steps. The first step is to estimate the density of the system. For this we run isotropic NPT simulation (where the number of particles, pressure and temperature remain fixed) for ~4ns at the concerned temperature and pressure. The damping coefficient for the temperature thermostat and pressure barostat was 1ps. Average convergence density is identified using the running average of density and the box density is then fixed to the average density by adjusting the box volume. Using this box as a starting point, several independent NVT simulations (where the Number of particles, Volume and Temperature remain fixed) are started in a protocol of heat→cool→production run. In order to have good statistics typically 20 such simulations are run. The heat/cool cycle ensures a different equilibrated system for each independent production run. Typically the heat and cool cycles are of 1ns each while the production run is ~8-16ns. Pressure tensor components are recorded during the production run. We used LAMMPS [11] package for all our simulations with default thermostat (Nose-Hoover chain) and barostat (implemented by Sinhoda *et. al.* [12]).

The Green-Kubo formalism has been used to estimate the viscosity from EMD simulations. The EMD approach considers a collection of energy conserving particles. The equation of motion is given by the Newton's Second Law:

$$m\ddot{\mathbf{r}} + \frac{\partial P}{\partial \mathbf{r}} = 0 \quad (1)$$

where P is the potential energy. Transport properties such as viscosity, elasticity, diffusion etc., may be approximately obtained through the EMD simulation by using the Green-Kubo relations. The basis of such approximation is the observation that the response due to a weak external excitation decays in the same way as a spontaneous fluctuation at equilibrium. Specifically for the shear viscosity, the Green-Kubo relation is given by:

$$\eta^{xy} = \frac{V}{k_B T} \int_0^\infty \langle \sigma^{xy}(0) \sigma^{xy}(t) \rangle dt$$

where $\langle \cdot \rangle$ denotes the ensemble average but computed using time average (based on the ergodicity assumption), V is the volume, k_B the Boltzmann constant, T the temperature, and σ^{xy} the xy component of the symmetric traceless stress tensor.

RESULTS AND DISCUSSION

Case 1: n-decane, n-dodecane and Their 50:50 Binary Mixture

Densities and viscosities of n-decane, n-dodecane and their 50:50 binary mixture have been reported by Dymond et. al. [13] up to 100°C, and pressures up to 5000 bar using a modified falling body viscometer. The experimental viscosities are shown in Figure 2 (the line is to guide the eye). As expected using mixing rules (see Appendix), the binary mixture viscosity falls roughly between the individual pure components. In this study we predict the densities and viscosities of the pure components and their binary mixture at 100°C and up to 2000 bar.

For simulations, we studied the systems using 100 molecules for pure components, i.e., n-octane and n-dodecane and in case of 50:50 mixture, we had 50 molecules of each n-octane and n-dodecane. The results are shown in Tables 1, 2, 3, Figures 2 and Figure 3.

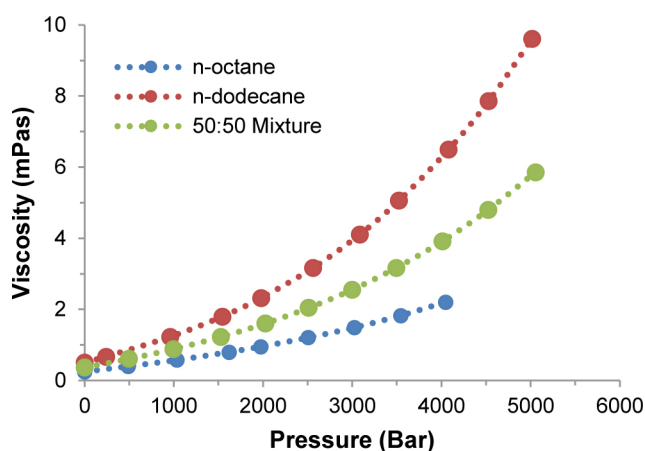


Figure 2. Experimental data [13] at 100°C. Red, blue and green circles indicate the viscosity of n-dodecane, n-octane and the 50:50 binary mixtures respectively.

As seen from the tables (Tables 1, 2, 3) and Figure 3, we were able to predict the densities within 2% relative to the experimental values using LOPLS interaction potential. Also the densities follow a linear addition rule (equation 3, where x_A and x_B are mole fractions of respective two components with densities ρ_A and ρ_B respectively) that can be used to predict densities of binary mixtures. In case of viscosities, pure component viscosities were predicted within 15% while the binary mixture viscosities were predicted within 25% for temperatures up to 100°C and pressures up to 2000 Bar (see Tables 1, 2, 3 and Figure 4).

$$\rho_m = x_A \rho_A + x_B \rho_B$$

(3)

There are many empirical correlations reported in literature quantifying pressure effects on viscosity. One of the most widely used correlations is given by the Barus [14] which is

$$\eta_p = \eta_0 e^{\alpha p} \quad (4)$$

where, η_p is the viscosity at pressure p , η_0 is the atmospheric viscosity, α is the coefficient and p is the pressure of concern. Barus relation is valid for pressure below 5000 bar. Thus for diesel fuel case we can rely on it. However, for applications in lubrication sciences where pressure can go beyond 10000 bar (1 GPa) alternative correlations are reported.

In literature, several empirical relations exist for predicting binary mixture viscosities from individual component viscosity and other physical properties. A simple one is Grunberg-Nissan model [15], which is widely used for predicting binary mixture viscosities. The Grunberg-Nissan model estimates the binary mixture viscosity by

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (5)$$

where, x is the mole fraction, subscripts 1 and 2 denote the mixture components. G_{12} is the interaction parameter which is characteristic of the mixture composition. G_{12} is a positive number and typically would lie between 0 and 2 for alkanes. For alkane binary mixtures G_{12} increases with the difference in carbon number of the pure components. The values tend to increase with an increase in pressure and the rate of increase becomes larger with the difference in carbon number. For a given system, G_{12} tends to decrease with increasing temperature, but the effect is small and becomes even less significant as the carbon numbers of the two pure components become closer. Using viscosity prediction models, binary mixtures viscosities of alkanes are generally predicted between the respective pure component viscosities (or in some cases, based on the value of interaction parameter, the binary mixture viscosity can be slightly higher than the respective pure component viscosities). Our predictions as well as the experimental data follow the expected behavior of Arrhenius relationships (see Appendix), or single parameter dependent relationships such as Grunberg-Nissan for viscosity predictions mentioned above and viscosities can be predicted after fixing the interaction parameter (positive number) for the molecules under study.

Table 1. Experimental [13] vs Simulation results (density and viscosity) for n-octane

T (C)	Press (Bar)	Density (gm/cc)		% error	Viscosity (mPas)		% error
		SIM	EXPT		SIM	EXPT	
25	1	0.6991	0.6985	0.1%	0.60	0.51	18%
100	1	0.6248	0.6355	-1.7%	0.29	0.25	16%
100	1036	0.7146	0.7215	-1.0%	0.63	0.57	10%
100	1977	0.7551	0.7594	-0.6%	1.07	0.95	13%