Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 158 (2019) 1700–1705

Energy Procedia

www.elsevier.com/locate/procedia

10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

Prediction of transport properties of fuels in supercritical conditions by molecular dynamics simulation

Cheng CHEN, Xi JIANG*, Yi SUI

School of Engineering & Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK

Abstract

Developing reliable method for predicting transport properties of fuels in supercritical environments has long been a matter of serious practical concern in combustion science and technology mainly due to the necessity of developing high-pressure combustion device. Two basic transport properties, *i.e.* shear viscosity and thermal conductivity, of methane and diesel surrogate fuels in conditions both near to and far from critical point are predicted. The computed values agree well with experimental results in supercritical conditions except for the deviation of shear viscosity in neighborhood of critical region due to critical divergences. The transport properties of *n*-Heptane in "Spray-H" and *n*-Dodecane in "Spray-A" conditions are also predicted using the same simulation settings with uncertainty quantification analysis. The statistical errors of density, viscosity and thermal conductivity are estimated to be less than 1.1%, 1.88%, 1.47% and 0.5%, 0.84%, 1.46% under these two conditions.

Keywords: Diesel surrogate fuel; Methane; Molecular dynamics simulation; Supercritical; Transcritical; Transport property

1. Introduction and Background

Supercritical (SC) combustion is a new concept of combustion technology in which fuels will be introduced into the combustion chamber in its SC state. SC combustion can lead to substantial reduction in ignition delay which aids in achieving shortest combustion duration. Therefore, higher fuel economy and less pollutant emissions can be achieved. To be specific, fuel injection and combustion at SC conditions have the potential of reducing emissions by 80% and increasing overall efficiency by 10% for a test internal combustion engine (ICE) [1]. Clearly, SC fuel

---

* Corresponding author. Xi JIANG. Tel.: +44 (0) 20 7882 5009.
E-mail address: xi.jiang@qmul.ac.uk

10.1016/j.egypro.2019.01.396

injection and combustion appears to be an attractive technology for the next-generation practical engine developments. Currently, an European Union Horizon 2020 Research and Innovation Programme has been approved to investigate the effect of 4500bar injection pressure and supercritical phase change of surrogate and real-world fuels enriched with additives [2]. In addition, current liquid-propellant rocket engine (LRE), gas turbines, scramjet engine and many advanced combustors operate supercritically or near critical conditions [3]. Representative LREs operate at a combustion chamber pressure greater than 6 MPa, which is higher than the critical pressures of methane (4.6 MPa) and kerosene (typically 2.3 MPa).

Although SC fuel injection and combustion have huge potentials in practical applications such as ICEs, predictions of diffusion-dominated mixing flow under SC conditions using computational fluid dynamics (CFD) methods are very challenging due to the lack of accurate fluid property data. In general, supercritical injection of liquid fuel at high-pressure and high-temperature conditions is not well understood. The fundamental issue with SC conditions is mainly associated with the extreme difficulties in obtaining the necessary data on the transport properties under these conditions, which are essential to CFD studies of such fluid systems. Near the critical point, transport properties of fluid undergo drastic changes and show unexplored transport properties like low viscosity, high diffusivity, low surface tension which will affect spray formation, spray penetration, fuel droplet size, injection timing, atomization and combustion characteristic. Therefore, developing reliable method for predicting the transport properties of fuels in SC environments has long been a matter of serious practical concern in combustion science and technology. The critical properties of pure materials can be obtained experimentally, but for the mixture, the experimental determination of critical data have high technical requirements. Furthermore, fluid property estimation obtained with a cubic equation of state (EoS) is known to be inaccurate when calculated at supercritical conditions or when the molecular weight of the component exceeds approximately 170 g/mol [4]. As an alternative to experimentation or EoS based methods, molecular dynamics (MD) simulations has become increasingly applied to calculate the thermophysical and thermochemical properties of supercritical fluid (SCF).

In this study, transport properties of methane and diesel surrogate fuels are calculated using All-Atom Optimized Potentials for Liquid Simulations (OPLS-AA) force field in MD simulation and compared with National Institute of Standards and Technology (NIST) data in conditions both near to and far from critical point. The transport properties of *n*-Dodecane in "Spray-A" and *n*-Heptane in "Spray-H" conditions, where no NIST or other experimental data available, are predicted with the statistical uncertainty analysed [5].

2. Theory and Computational Methods

There have been a number of different atomistic simulation methods developed for computing the transport property of liquids [6]. Due to its simplicity, the Green-Kubo (G-K) method based on equilibrium molecular dynamics simulations is used in this study. The G-K relationships relate equilibrium fluctuations of fluxes to corresponding phenomenological coefficients L_{ij}.

$$L_{ij} = \frac{V}{3k_B}\int_0^\infty \left\langle J_i(t) J_j(0) \right\rangle_{eq} dt \tag{1}$$

Given a microscopic and instaneous expression for fluxes J_i(t), one can compute L_{ij} from a single equilibrium run. Within the framework of irreversible process, L_{ij} can therefore be connected with the transport coefficients. Shear viscosity η and thermal conductivity λ can be computed at equilibrium from the following expressions:

$$\eta = \frac{V}{k_B T}\int_0^\infty \left\langle \sigma_{xy}(t)\sigma_{xy}(0) \right\rangle \qquad \lambda = \frac{V}{3k_B T^2}\int_0^\infty \left\langle J_q(t) J_q(0) \right\rangle dt \tag{2}$$

where V is system volume, k_B is Boltmann constant, T is temperature, σ_{xy}(t) and J_q(t) are pressure tensor component and heat flux.

All the MD simulations are performed in LAMMPS (Large-scale Atomic Massively Parallel Simulator) package [7]. The energy of the system is calculated using OPLS-AA force field with fully flexible sites models according to equation:

$$U_{OPLS} = \sum_{bonds} k_r (r - r_0)^2 + \sum_{bonds} k_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} \sum_{l=1}^{3} k_l (1 - (-1)^l \cos l\phi) \tag{3}$$

where k_r, k_θ, k_l are force constraints, and f_{ij} is "fudge factor" of 0.5 for atoms 3 or more bonds apart; 1.0 otherwise [8]. The parameters for stretching, bending, and torsions are taken from the OPLS-AA force field without modification. The interaction between sites on different molecules and between the sites separated by more than three bonds in the same *n*-alkane molecule is described by a Lennard-Jones (LJ) potential. The Lorentz-Berthelot combining rules $\sigma_{ij}=(\sigma_{ii}\sigma_{jj})^{1/2}$ and $\varepsilon_{ij}=(\varepsilon_{ii}\varepsilon_{jj})^{1/2}$ are used for interactions between an end site and an internal site. Cut-off distances for L-J interactions and Coulombic interactions are both taken to be 1.2 nm. The long-range Coulombic interactions are calculated using particle-particle-particle mesh (PPPM) solver which evaluates Fourier series directly with a desired relative error in forces of 1×10^{-4}. The minimization of energy is carried out through steepest descent method, And Newton's equations of motion are solved using a fifth-order Gear predictor-corrector numerical intergrator. Periodic boundary conditions are applied in three directions for all simulations. Temperature is controlled using the Nosé-Hoover thermostat with a fixed temperature-damping factor equal 100. All simulations are performed in the isobaric-isothermal (NPT) ensemble with system of 1024 molecules in a cubic box. The initial velocities are assigned following a Maxwell-Boltzmann distribution at each temperature. To avoid explosions, the system has a 4-step equilibration process (expansion, minimization, reorientation, compression), followed by a 1 ns equilibration run, whose trajectories are used to compute viscosity and thermal conductivity. The configurations of all the molecules for further analyses are stored every 5 time_step (1fs) which is small enough for the tick of any time auto-correlation functions.

3. Predictions and discussion

The main objective of this research is to develop method for predicting the transport properties of fuels in SC conditions, the simulations have been performed using pure methane, *n*-Heptane and *n*-Dodecane at conditions both near to and far from critical point. Table 1 and table 2 show the critical point, simulation results and relative deviation (RD), respectively.

Table1: critical point of methane and diesel surrogate fuels

Substance	T_B(K)	T_c(K)	P_c(MPa)	ρ_c(g/ml)
methane	111.67	190.56	4.60	0.16
n-Heptane	371.53	540.13	2.73	0.23
n-Dodecane	489.30	658.10	1.82	0.23

3.1. Results

Table 2: results and relative deviation of transport properties of methane and diesel surrogate fuels at SC condition in NPT ensemble

Substance	T(K)	P(MPa)	η (μPa·s)			λ (W/K)		
			NIST	MD	RD%	NIST	MD	RD%
Methane	203.15	6	13.31	26.89	102.02	54.79	70.49	28.65
		30	46.37	57.49	23.98	119.04	110.76	-6.96
		100	78.49	99.35	26.57	185.79	156.12	-15.96
	573.15	10	19.63	14.56	-25.83	86.85	58.20	-32.99

		30	22.24	22.61	1.66	95.79	90.99	-5.01
		100	32.36	39.62	22.44	127.22	123.17	-3.18
n-Heptane	550.15	3	20.88	46.54	122.89	50.19	88.77	76.86
		10	73.85	68.04	7.86	87.90	94.11	7.06
		30	107.70	103.01	-4.35	105.87	118.76	12.17
	590.15	3	16.09	27.18	68.92	48.53	81.19	67.29
		10	58.80	59.36	0.95	82.78	90.37	9.16
		30	93.10	85.10	-8.59	103.59	128.68	24.22
n-Dodecane	660.15	3	47.30	56.87	20.23	69.98	105.12	50.21
		10	83.41	72.54	-13.03	80.37	108.21	34.63
		30	139.09	108.05	-22.31	96.87	117.62	21.42
	695.15	3	24.52	44.97	83.40	67.73	87.02	28.48
		10	67.69	64.22	-5.13	77.79	101.81	30.88
		30	121.44	102.08	-15.94	94.61	104.39	10.34

Clearly, at the temperatures and pressures far from the critical point, the agreement between the computed and NIST values is satisfactory, whereas the agreement is not as good near the critical point, and particularly evident for the viscosity coefficient. This is mainly due to the drawback of equilibrium molecular dynamics simulations and critical divergences in the critical point, that is, density fluctuation of fluid near the critical point is infinite and the properties of SCF can be easily adjusted by small variations of the average temperature and pressure. Equilibrium molecular dynamics simulation cannot capture the divergences in the critical point. Some research has shown that even far from the critical point, the properties divergences at the critical point can be felt and induce unexpected dynamic responses [9].

It is worth noting that all of the results presented in this paper are obtained using only one set of OPLS-AA parameters [10], which had been optimized for calculating transport properties at lower temperatures and pressures. More accurate results for long hydrocarbons at higher pressure and temperature values can be obtained by making use of parameters that have been optimized and improved for those conditions [11].

3.2. Prediction and uncertainty analysis

In order to establish a coherent database for engine combustion model validation, the Engine Combustion Network (ECN) carried out a serials of experiments at well-defined standard conditions (in particular at "Spray-A" boundary conditions: 900K, 6MPa and "Spray-H" conditions: 1000K, 4.3MPa) [12]. Therefore, predictions of transport properties of *n*-Dodecane at "Spray-A" and *n*-Heptane at "Spray-H" combustion conditions where there are no NIST and experimental data are valuable. (See http://www.sandia.gov/ecn/ for a complete description of the "Spray A" & "Spray H" condition).

MD simulation results may be subject to both systematic and statistical errors [13]. Whereas systematic errors should be eliminated by using the appropriate simulation technique and by correctly performing the simulation, statistical errors are unavoidable and have to be properly quantified [14]. The uncertainties of predicted values are estimated using blocking average method [15]. In this method, the following equation is used to estimate the overall standard deviation in the simulation:

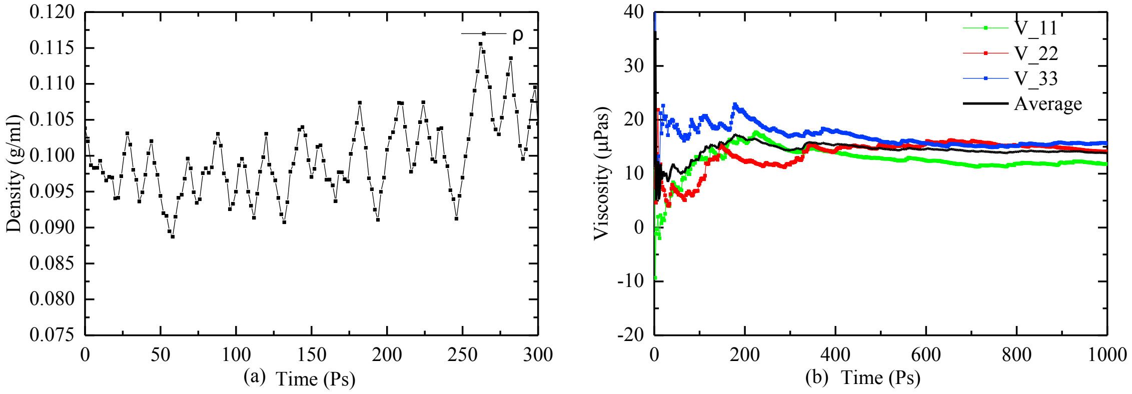
$$RSD = \frac{\sigma(\overline{A})}{\sqrt{N_B - 1}} \tag{4}$$

where N_B is block number and $\sigma(\overline{A})$ is the standard deviation among the block average.

Table 3: The calculated density, shear viscosity and thermal conductivity and their relative standard deviation (RSD) of statistical errors

Result	*n*-Heptane			*n*-Dodecane		
	ρ (g/ml)	η (μPa·s)	λ(W/K)	ρ (g/ml)	η (μPa·s)	λ(W/K)
MD simulation	0.0996	13.82	47.63	0.477	32.77	28.06
RSD%	1.10	1.88	1.47	0.50	0.84	1.46

Fig. 1 and Fig. 2 show the MD simulation results of *n*-Heptane in "Spray-H" and *n*-Dodecane in "Spray-A" conditions and Table 3 shows that the statistical errors of density, viscosity and thermal conductivity are estimated to be less than 1.1%, 1.88%, 1.47% and 0.5%, 0.84%, 1.46%, respectively.



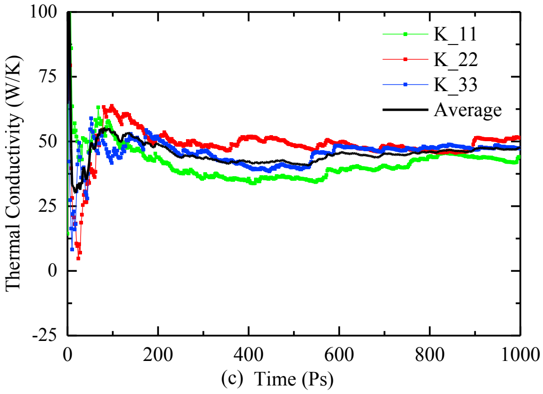
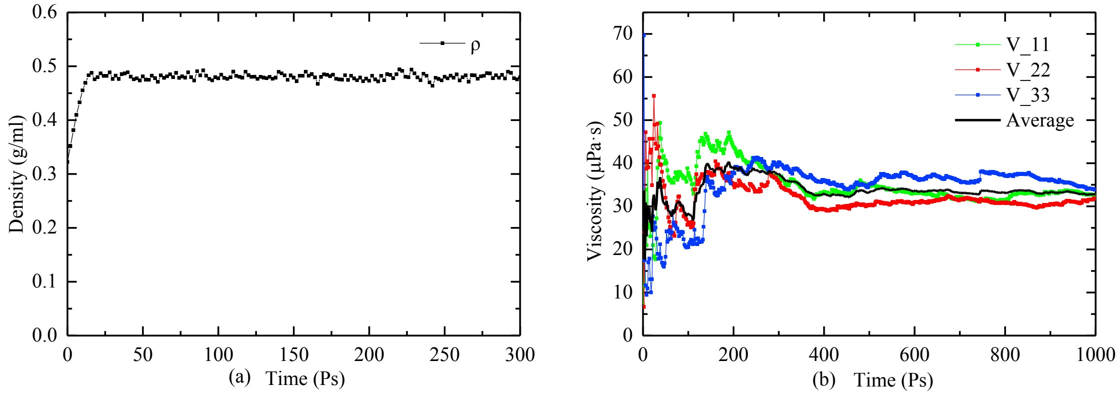


Fig. 1: Result of density (a), viscosity (b) and thermal conductivity (c) calculating using G-K relation based on three independent 1ns trajectories generated for *n*-Heptane at "Spray-H" conditions (T=1000K, P=4.3MPa).



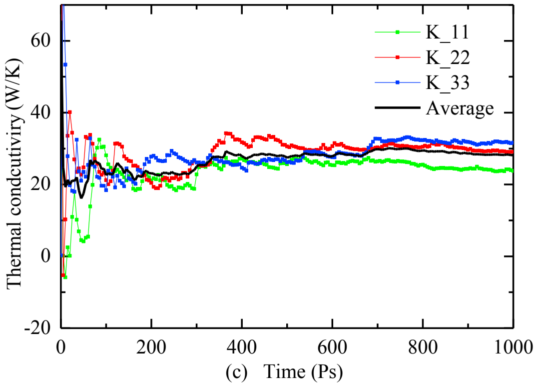


Fig. 2: Result of density (a), viscosity (b) and thermal conductivity (c) calculating using G-K relation based on three independent 1ns trajectories generated for *n*-Dodecane at "Spray-A" conditions (T=900K, P=6MPa).

4. Conclusions

In the present study, Green-Kubo method based on equilibrium molecular dynamic simulation with OPLS-AA force field is employed to provide predictions of transport properties of methane and diesel surrogate fuels in SC conditions. The computed properties are in good agreement with experimental data in conditions far from the critical point. But in neighborhood of the critical point, large deviation is observed due to critical divergences and density fluctuation. The density, shear viscosity and thermal conductivity of *n*-Heptane in "Spray-H" and *n*-Dodecane in "Spray-A" conditions where no experimental data available are predicted using the same simulation settings with the statistical errors quantified as less than 1.10%, 1.88%, 1.47% and 0.50%, 0.84%, 1.46%, respectively.

References

[1] Lin R. Issues on clean diesel combustion technology using supercritical fluids: thermophysical properties and thermal stability of diesel fuel. Syracuse University; 2011.

[2] Mallepally RR, Bamgbade BA, Rowane AJ, Rokni HB, Newkirk MS, McHugh MA. Fluid properties at high pressures and temperatures: Experimental and modelling challenges. Journal of Supercritical Fluids. 2017; 134:33-40.

[3] Nwobi O, Long L, Micci M, Nwobi O, Long L, Micci M. Molecular dynamics studies of transport properties of supercritical fluids. 35th Aerospace Sciences Meeting and Exhibit. 1997; 1-11.

[4] Saxena SK. Thermodynamic data: systematics and estimation. Springer; 2012.

[5] Stubbs JM. Molecular simulations of supercritical fluid systems. Journal of Supercritical Fluids. 2016; 108:104-122.

[6] Fernandez G, Vrabec J, Hasse H. A molecular simulation study of shear and bulk viscosity and thermal conductivity of simple real fluids. Fluid Phase Equilibria. 2004; 221:157-163.

[7] Plimpton S. Fast parallel algorithms for short-range molecular dynamics. Journal of Computational Physics. 1995; 117:1-19.

[8] Paulechka E, Kroenlein K, Kazakov A, Frenkel M. A systematic approach for development of an OPLS-like force field and its application to hydrofluorocarbons. Journal of Physical Chemistry B. 2012; 116:14389-14397.

[9] Carlès P. A brief review of the thermophysical properties of supercritical fluids. Journal of Supercritical Fluids. 2010; 53:2-11.

[10] Jorgensen WL, Maxwell DS, Tirado-Rives J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. Journal of the American Chemical Society. 1996; 118:11225-11236.

[11] Siu SW, Pluhackova K, Böckmann RA. Optimization of the OPLS-AA force field for long hydrocarbons. Journal of Chemical Theory and Computation. 2012; 8:1459-1470.

[12] Malbec L-M, Egúsquiza J, Bruneaux G, Meijer M. Characterization of a set of ECN spray A injectors: nozzle to nozzle variations and effect on spray characteristics. SAE International Journal of Engines. 2013; 6:1642-1660.

[13] Cailliez F, Pernot P. Statistical approaches to forcefield calibration and prediction uncertainty in molecular simulation. Journal of Chemical Physics. 2011; 134:0541241-05412414.

[14] Raabe G. Molecular Simulation Studies on Thermophysical Properties. Springer; 2017.

[15] Flyvbjerg H. Error estimates on averages of correlated data. Journal of Chemical Physics. 1998; 91:461-466.