AFRL-OSR-VA-TR-2013-0168

Chemistry and Transport Properties for Jet Fuel Combustion

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April 2013
Final Report

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AF OFFICE OF SCIENTIFIC RESEARCH (AFOSR)
ARLINGTON, VIRGINIA 22203
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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 11/30/2012	**2. REPORT TYPE** Final Report	**3. DATES COVERED** *(From - To)* 12/1/2008-11/30/2012

4. TITLE AND SUBTITLE

(U) Chemistry and Transport Properties for Jet Fuel Combustion

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-09-1-0021

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)

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5d. PROJECT NUMBER
2308

5e. TASK NUMBER
BX

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Office of
Scientific Research
875 North Randolph Street
Suite 325, Room 3112
Arlington VA 22203-1768

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-OSR-VA-TR-2013-0168

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release. Distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Combustion modeling is an essential tool for the prediction of flame characteristics as well as for the optimal design of combustors. Although, chemical kinetic mechanisms of hydrocarbons have been widely studied, molecular transport data of those species, especially for molecules with a large number of atoms, have not yet experienced similar focus. The Chapman-Enskog solution of the Boltzmann transport equation (C-E), whose validity is limited to low-density gases with the assumption of spherical interactions between molecules, produces a mathematical expression for mutual diffusion coefficients. This equation, however, has been extensively employed to determine transport properties of significant non-spherical molecules in high temperature conditions. In addition, the C-E equation is difficult to apply since it requires the knowledge of collision integrals, collision diameters, and energy well depth, all of which are experimentally determined quantities for each pair of molecules. The goal of this study has been to determine accurate diffusion coefficients of hydrocarbons using all-atom molecular dynamics (MD) simulations and to propose new correlations to improve the prediction of diffusion coefficients for molecules with non-spherical symmetry. The effects of molecular structure on diffusion have been determined for components of jet fuel surrogates. The results have been compared with available experimental data.

15. SUBJECT TERMS
Combustion Kinetics, Jet Fuels, Reaction Mechanism, Transport Properties.

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Chiping Li
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	SAR		**19b. TELEPHONE NUMBER** *(include area code)* 703-696-8478

Grant/Contract Title: CHEMISTRY AND TRANSPORT PROPERTIES FOR JET FUEL COMBUSTION
Grant/Contract Number: FA9550-09-1-0021
P.I.: Angela Violi
Affiliation: University of Michigan

Final Report: 2008-12-01 to 2012-11-30

Statement of Work

The primary objectives of this proposal have been to establish fundamental chemical and physical properties of jet fuel components that can be used to develop a comprehensive and extensible kinetic model for the combustion of practical jet fuels as well as their surrogates. Specifically, the objectives were **(a)** to identify reaction pathways for the combustion of jet fuel surrogates; **(b)** to develop detailed kinetic models for these compounds; **(c)** to compute the transport properties of jet-fuel surrogates and **(d)** to develop a database of transport properties that can be implemented in current simulation packages, such as CHEMKIN. The development of the kinetic mechanisms was coordinated with the effort carried out by the research team led by Prof. Egolfopoulos, within the MURI award.

Major Accomplishments:

The major achievements obtained over the last years can be summarized as follows:

1. Determination of accurate values of diffusion coefficients for JP8 surrogates. Currently the values used in combustion codes are obtained from the kinetic theory that is valid for spherical molecules. This approximation causes great discrepancies – it has been demonstrated that for example 10% differences in diffusion coefficients of n-dodecane flame can cause 50K difference in ignition temperature.

Molecular Dynamics simulations in combination with ab initio methods were used to determine the chemistry and transport processes of classes of n-, iso-, and cyclo-paraffins, and their mixtures. We included also the class of aromatics – initially not listed in the SOW.

2. Development of a model that correlates the morphology of molecules with diffusion coefficients. This new equation can be used in available combustion models to improve their predictive capability.

3. Co- development of JetSurf kinetic model – version 2 released Sep 2010:
Authors:
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A. Violi, *University of Michigan*

4. Determination of new reaction pathways and rates for classes of reactions important to combustion modeling. H abstraction by H, OH, CH3 and O from alkane, cycloalkane and aromatic families. For each family of compounds we looked at molecules with various numbers of atoms. For example for the alkanes, we studied H abstractions from 16 molecules for a total of 16*4 reactions.

5. Development of a Kinetic Sub-mechanism for cyclo-alkanes. In addition to H abstractions, we looked at unimolecular decomposition pathways using ab initio methods and determining rates as function of Pressure.

6. New findings from our group in terms of reactions and rates have been implemented in a newer version of JetSurf and it has been used to predict experimental data collected in shock tubes by Prof. Hanson – results are in Paper 2 – in list of publications.

Archival publications (published) during reporting period:

1. V.T. Dillstrom, P.Elvati, A. Violi “Diffusion properties of cycloalkanes” Journal of Chemical Physics, in preparation (expected submission Jan 20 2012).

2. V. T. Dillstrom, P. Elvati, A. Violi “Gas Phase Molecular Diffusion: A review” Progress in Energy and Combustion Science, Invited publication 2012.

3. A. A. Mohamad, V. T. Dillstrom, J. K. Lai, A. Violi, “Ab Initio Investigation of the Thermal Decomposition of n-Butylcyclohexane, J. Comput. Chem., submitted.

4. K. C. Lin, J. Y. Lai, A. Violi “The role of the methyl ester moiety in biodiesel combustion: A kinetic modeling comparison of methyl butanoate and n-butane” Fuel: 92, 16-26 (2012).

5. K. Chae, P. Elvati, A. Violi “Effect of Molecular Configuration on Binary Diffusion

Coefficients of Linear Alkanes" Journal of Physical Chemistry B: 115(3), 500-506, (2011).

6. K. Chae, A. Violi, "Mutual diffusion coefficients of heptane isomers in nitrogen: A molecular dynamics study" The Journal of Chemical Physics 134 (4), Article Number: 044537 (2011).

7. Farooq, D. F. Davidson, R. K. Hanson, L. K. Huynh, A. Violi "An Experimental and Computational Study of Methyl Ester Decomposition Pathways using Shock Tubes", Proc. Combust. Inst. 32(1): 247-253 (2009).

Thesis:

K. Chae, "Mass Diffusion and Chemical Kinetic Data for Jet Fuel Surrogates" PhD Thesis, Mechanical Engineering, University of Michigan, 2010.

Conference Proceedings and Posters:

1. V.T. Dillstrom. P. Elvati, A. Violi "Molecular Diffusion of Alkanes", Int. Symp on Combustion, July 29-Aug 3 2012, Warsaw, Poland.

2. M.A.Ali, A. Violi "Ab Initio Investigation of the Thermal Decomposition of n-Butylcyclohexane", Int. Symp on Combustion, July 29-Aug 3 2012, Warsaw, Poland.

3. M.A.Ali, A. Violi "Theroretical study of reaction pathways of butyl-cyclohexane" 22nd International Symposium on Gas Kinetics", June 18-22, 2012, Boulder Colorado.

4. D. Kim, P. Elvati, J. Martz, A. Violi "Development of comprehensive JP-8 surrogate for heavy duty compression ignition engine" 18th Annual ARC Conference "Powering future mobility" May 21-22, 2012, Ann Arbor, Mi.

5. K. Lin, J. Lai, A. Violi "Insights on the effects of fuel composition on reaction pathways", 6th US National Meeting of the Combustion Institute, Ann Arbor, MI, 17-21 May 2009.

6. K. Chae, A. Violi "Binary mass diffusion coefficients of polyatomic gases - investigation on the effects of alkane chain length on mass diffusivity", 6th US National Meeting of the Combustion Institute, Ann Arbor, MI, 17-21 May 2009.

Other activities:

Ph.D. Students

Kyungchan Chae, “Transport properties of jet fuels” *Graduated* September 2010.

M.S. Students Advised

Greg Wagner: Mechanical Engineering, University of Michigan
Project: “Transport Properties of Hydrocarbons” Period: September 2009 – May 2010

Undergraduate projects Directed

(UG 1) Title: “Molecular Dynamics simulations of hydrocarbons at high temperature”
Mr. Michael Baskins Period: 1/2009 – 5/2009

(UG 2) Title: “Kinetics of hydrocarbon fuels”
Mr. Nickolas Burtch Period: 1/2009 – 12/2009

(UG 3) Title: “Transport of Hydrocarbons”
Mr. Nanut panpreck Period: 5/2009 – 12/2009

(UG 4) Title: “Transport properties of alkanes”
Nattasit DancholvichitPeriod: 9/2010 – 4/2011

(UG 5) Title: “Transport properties of cyclo-alkanes”
Mrs. Jessica Devriese Period: 9/2010 – 4/2011

(UG 6) Title: “Diffusion coefficients of aromatics”
Mrs. Jessica Devriese Period: 5/1/2012-11/30/2012

Research Highlights

Work on transport was selected as research highlight by AFOSR in 2010.

Invited Publication of Review Article on Transport, Progress in Energy and Combustion, 2012.

Connection to AFOSR goals: The proposed research has produced a comprehensive reaction model that includes kinetic modules for the surrogate components and implementation of advanced transport. The impact of this work – especially for the results on diffusion coefficients will affect all the kinetic mechanisms used in the combustion community since – as today – there are no accurate data for the diffusions of non-spherical molecules.

Executive Summary:

Combustion modeling is an essential tool for the prediction of flame characteristics as well as for the optimal design of combustors. Mass diffusion coefficients and chemical kinetic mechanisms are essential input data to investigate complex flame behaviors, such as flame speed, heat and mass transfer, and ignition characteristics. Although, chemical kinetic mechanisms of hydrocarbons have been widely studied,[1-3] molecular transport data of those species, especially for molecules with a large number of atoms, have not yet experienced similar focus.[4-6]

Over the years, kinetic theory for polyatomic gases has been formulated in different ways. The Chapman-Enskog solution of the Boltzmann transport equation (C-E) produces a simple mathematical expression for mutual diffusion coefficients.[7] Hirschfelder et. al. followed the Chapman–Enskog approach, combined with the Lennard–Jones (LJ) 12 – 6 intermolecular potential function, and suggested the Hirschfelder–Bird–Spotz (HBS) equation for mutual mass diffusion coefficients[8]

$$D_{12} = \frac{3}{8}\frac{\sqrt{(k_B T)^3/(2\pi m_{12})}}{n\sigma_{12}^2 \left\langle \Omega^{(1,1)*} \right\rangle}$$

where k_B is the Boltzmann constant, T is the temperature of a system, m_{12} is the reduced mass of the pair components, n is the average number density, σ_{12} is the collision diameter of two species and $\Omega^{(1,1)^*}$ is the collision integral and it depends on the reduced temperature. The main disadvantage of this equation is the difficulty encountered in evaluating the collision diameter, σ_{12} , and potential energy well depth, ε_{12} . These two parameters are usually obtained from viscosity measurements.[8] However, only a limited amount of data is available for polyatomic molecules. Therefore, the correlations of corresponding states of Tee et al. are frequently employed to estimate the parameters for fluids. [9]

The validity of above equation is limited to low density gases with the assumption of spherical interactions between molecules. Despites these limitations, the equation above has been extensively employed to determine transport properties of significant non-spherical molecules in high temperature conditions.

In addition, the C-E solution to the Boltzmann transport equation is not applicable for many systems because they require the knowledge of collision integrals, collision diameters, and energy well depth, all of which are experimentally determined quantities for each pair of molecules. The dearth of experimental data severely limits the quantity of systems for which analytical transport equations are viable. Because of the severe limitations of gas kinetic theories, the major advantage of computational approaches such as MD is its ability to simulate systems where experimental data are not available.

Recent investigations, however, have reported the importance of mass diffusion coefficients in flame modeling.[10-13] H_2/air flame simulations showed up to 30%

difference in extinction strain rate when different transport formulations were employed.[10] Modeling of non-premixed flames of hydrocarbons have highlighted the importance of size and mobility of molecules on the extinction strain rates; as the size of molecules decreases, resistance to extinction strain rate increases.[12] Sensitivity analyses of ignition, laminar flame speed and extinction strain rates have reported that the sensitivity of diffusion could be on the same order or larger than chemical kinetics.[10,11,13] The goal of this study has been to determine accurate diffusion coefficients of hydrocarbons using all-atom Molecular Dynamics (MD) simulations and to propose modifications to the HBS equation to improve the prediction of diffusion coefficients for molecules with non-spherical symmetry. One of the main goals of this study is to identify and quantify the effect of molecular structure on diffusion. All-atom Molecular Dynamics simulations are employed to overcome the limitations of the C-E theory with spherical potentials and provide an explicit way to compute diffusion coefficients of polyatomic molecules.

As systems of interest, we focused on alkanes (from methane, CH_4 to hexadecane, $C_{16}H_{34}$) , the isomers of alkanes (isomers of heptane), cycloalkanes, and aromatics.

Approach

One major advantage of individual molecular measuring methods is the lack of obstacles between simulation output and calculation of the diffusion coefficient. Given the results of a simulation that tracks each molecule in the specified system, one can obtain the macroscopic diffusion coefficient with relatively simple expressions like the

Green-Kubo (G-K) formula, [14] which can determine mass diffusion coefficients in systems at equilibrium state from microscopic fluctuations.[15] The G-K formula defines both self and binary diffusion coefficients, the former is an ensemble average of the velocity auto correlation function, the latter is defined as a combination of the ensemble average of velocity auto correlation and cross correlation functions.[16] The binary diffusion coefficient is described by[17]

$$D_{12} = Q\left[x_2 D_1 + x_1 D_2 + x_1 x_2\left(\frac{f_{11}}{x_1^2} + \frac{f_{22}}{x_2^2} - 2\frac{f_{12}}{x_1 x_2}\right)\right]$$

$$D_\alpha = \frac{1}{3}\int_0^\infty \langle \vec{u}_i^\alpha(t) \cdot \vec{u}_i^\alpha(0)\rangle dt$$

$$f_{\alpha\alpha} = \frac{1}{3}\int_0^\infty \langle \vec{u}_i^\alpha(t) \cdot \vec{u}_j^\alpha(0)\rangle dt$$

$$f_{\alpha\beta} = \frac{1}{3}\int_0^\infty \langle \vec{u}^\alpha(t) \cdot \vec{u}^\beta(0)\rangle dt$$

where the angle brackets denote an ensemble average, D_α is the time integral of the velocity auto correlation functions of species α, $\vec{u}^\alpha$ and $\vec{u}^\beta$ are the velocity vectors of species α and β, respectively, $f_{\alpha\alpha}$ and $f_{\alpha\beta}$ are the time integrals of the velocity cross correlation function between the same species and between species α and β, respectively, x_α is the mole fraction of species α, and Q is a thermodynamic factor related to the compositional derivative of chemical potential. Employing these G-K relations to calculate the diffusion coefficient of a simulated system is relatively straightforward and simple. This ease of use is a significant advantage to individual molecular measuring simulations.

Molecular Dynamics

Molecular dynamics, in theory, is a relatively simple idea predicated on basic Newtonian dynamics. MD provides a method to calculate diffusion properties, effective especially in systems of interest wherein the temperatures, or pressures, or both, are extreme because experiments with extreme conditions are impracticable. Furthermore, MD is an effective method to simulate molecular systems where the particles of interest are large enough to neglect quantum effects, such as electron-electron interaction and electron-atom interaction. Electron movement relative to nuclei is ignored for the sake of computational efficacy, save for *ab-initio* MD. This simplification is especially valid and useful for hydrocarbon systems typical in combustion environments.

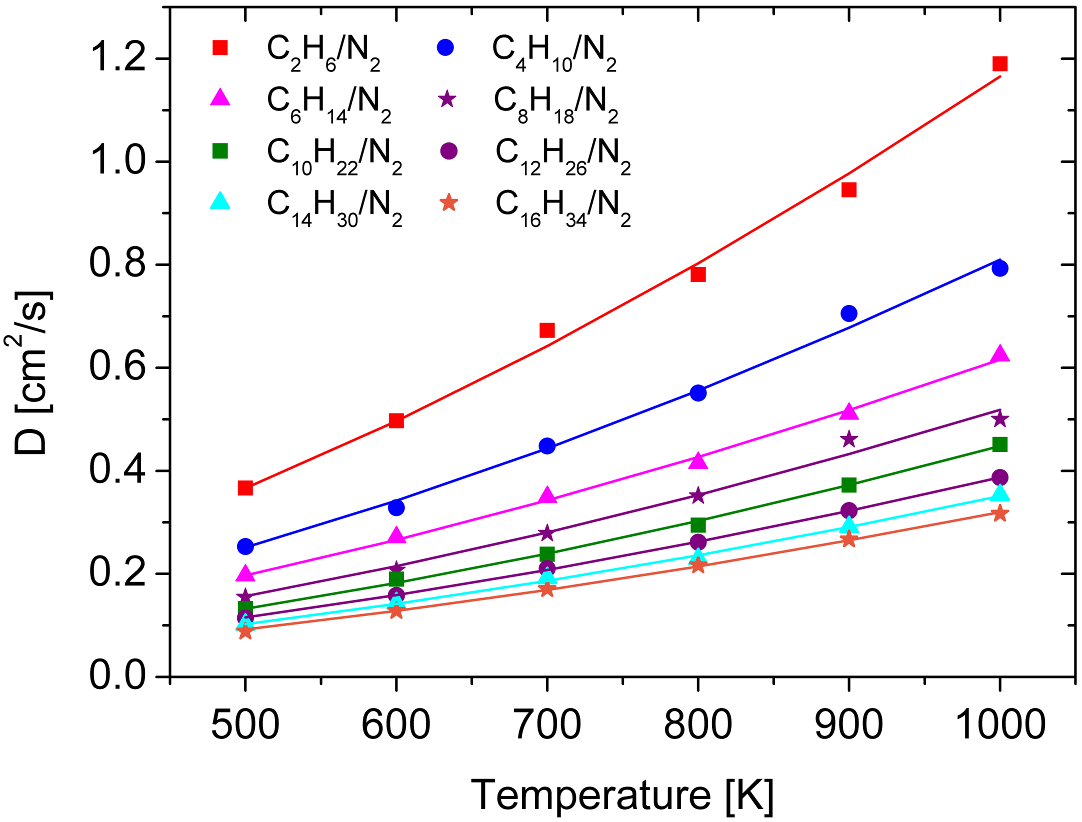
More details about the methodology employed for this work are reported elsewhere.[18-19]

Results

Below are reported the results for alkane species. The work done for the other families of compounds are reported in journal publications as well as PhD thesis.

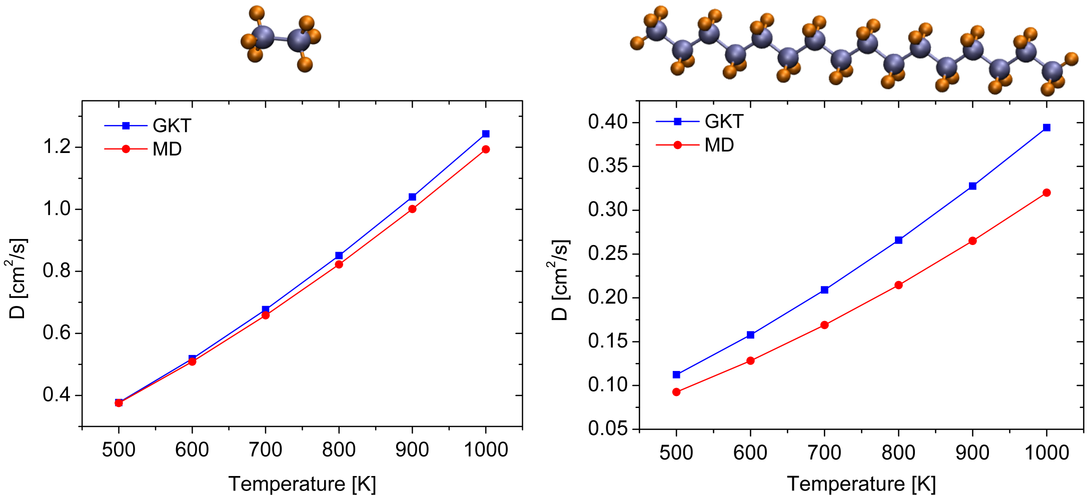
Our group has noted[18-19] that C-E theory overestimates the diffusion coefficients of linear and branched alkanes, cycloalkanes, and aromatics. Because C-E gas kinetic theory relies on the assumption of hard sphere collisions, the less spherical a molecule is, the more C-E theory overestimates the diffusion coefficient. The larger the alkanes are, the larger the discrepancy between C-E diffusion coefficients and MD diffusion coefficients; as the molecules deviate from a spherical shape, analytical methods become less accurate.

MD results for the binary diffusion coefficients of alkanes from methane CH_4 to hexadecane, $C_{16}H_{34}$ presented in the figure below.



As the number of methyl groups increases, the diffusion coefficients decrease. Moreover, the difference in diffusion coefficients among mixtures becomes larger as temperature increases. Experimental measurements of mutual diffusion coefficients for gas mixtures at 1 atm.

The figure below reports the diffusion coefficients for two mixtures of hydrocarbons in nitrogen (ethane on the left panel and dodecane on the right), obtained using MD simulations and the HBS equation.



This comparison is meant to demonstrate that the deviation in diffusion values originates from the utilization of monatomic spherical potentials. For the C_2H_6/N_2 mixture, the agreement between MD simulations and HBS values is good. The same comparison carried out for the $C_{16}H_{34}/N_2$ mixture shows significant differences between the two methods. The average deviation is around 17%, with MD underestimating the diffusion values compared with the HBS equation. The overall result suggests that the HBS approach produces values of the diffusion coefficients similar to MD when the molecules have spherical symmetry, i.e. CH_4 or C_2H_6. In other words, using single body interaction potentials is not appropriate for molecules that have non-spherical structures.

In order to quantify the difference in diffusion values between the two approaches, we searched for a geometric factor that could represent the molecular structures obtained from MD simulations and at the same time could be compared with a collision diameter (σ). For this purpose, we computed the radius of gyration (R_g) of each hydrocarbon molecule from MD simulations using the following relation:

$$Rg = \sum_{\alpha=1}^{3} I_{\alpha\alpha}$$

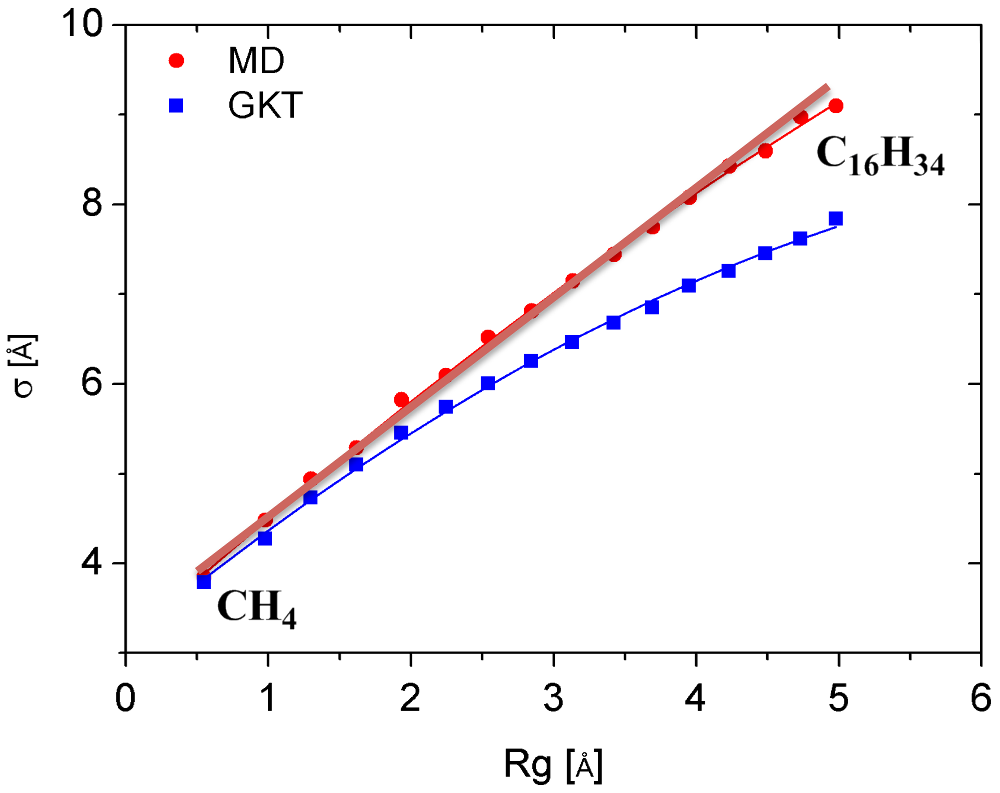
where $I_{\alpha\alpha}$ denotes the moments of inertia of principal axes.

An important difference between σ and Rg is the temperature dependence of the latter, which makes the analysis of the diffusion trends complex. However, the computed values of R_g in the temperature range of 500 – 1000 K did not vary significantly.

As the length of the chain of alkanes increases, the radii of gyration and collision diameters also increase. The similarity depicted in the figure demonstrates that R_g is related to σ, as expected since both characterize the molecular size, yet the radius of gyration imbeds geometric factors that are not captured by the collision diameter of a spherical potential function. The CE theory can be used to compute diffusion coefficients of non-spherical polyatomic molecules only when the collision diameters (σ_{CE}) are linearly related to the radii of gyration (Rg). The second-order fitting curve represents the deviation from sphericity of the molecules.

Using the values of diffusion coefficients from MD simulations, we determined new collision diameters (σ_{MD}) for the hydrocarbon molecules. For the energy well depth (ε), we used the same values employed in the HBS equation, since the inverse square of σ is proportional to diffusion coefficients. As shown in the Table blow, 10% perturbation of σ causes around 11.3% deviation from the original diffusion values. On the other hand, the same amount of perturbation of ε produces only 1.5% deviation. This result confirms that σ has a dominant effect on determining diffusion values when compared with the energy well depths.

The comparison between σ_{MD} and σ_{CE} for linear alkanes in the figure below, shows that the HBS equation produces larger deviations as the number of methyl groups in the chain increases, raising concerns regarding the ability of CE theory coupled with spherical potentials, to produce reliable diffusion coefficients for polyatomic molecules.



The dependence on Rg represents a simple way to take into account the effect of molecular configurations when using the CE theory with spherical potentials.

$$\sigma_{MD} = \frac{3.1+1.4R_g - 4.6E-2R_g^2}{3.1+1.3-7.8E-2R_g^2}\sigma_{CE}$$

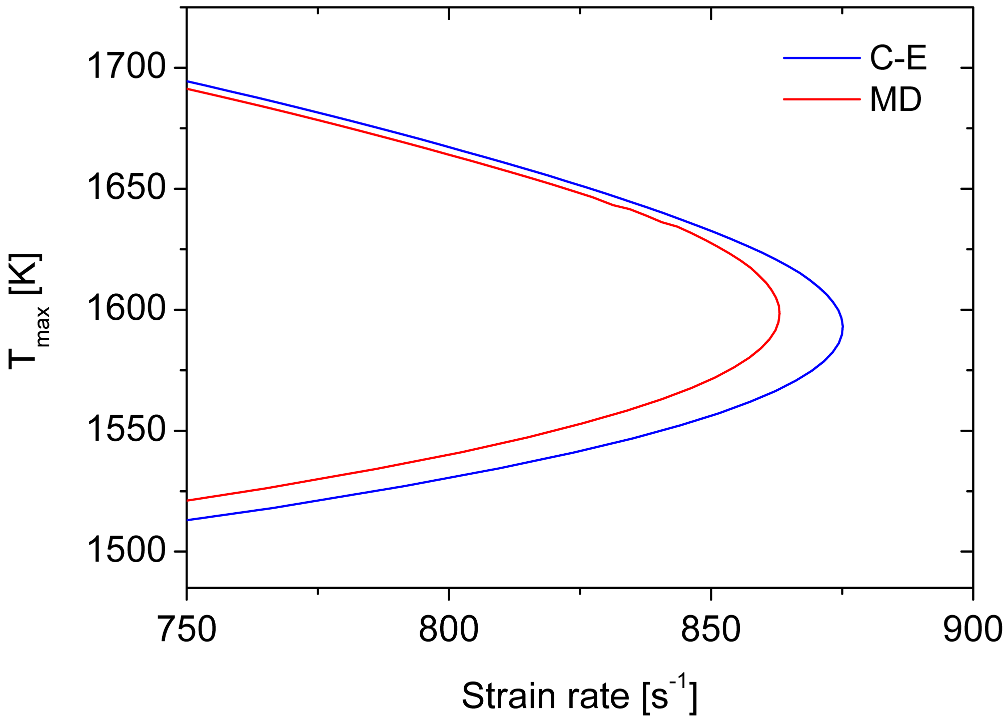
The results are summarized in tables showing the values of Lennard-Jones parameters that can be used in available combustion models. The table below reports the values for the family of alkanes.

Species	σ [Å]	ε/k_B [K]	Species	σ [Å]	ε/k_B [K]
CH_4	3.771	154.9	C_9H_{20}	6.637	649.6
C_2H_6	4.515	227.9	$C_{10}H_{22}$	6.997	681.2
C_3H_8	4.915	315.6	$C_{11}H_{24}$	7.184	685.0
C_4H_{10}	5.314	356.3	$C_{12}H_{26}$	7.482	688.9
C_5H_{12}	5.648	425.2	$C_{13}H_{28}$	7.591	738.1
C_6H_{14}	5.993	457.1	$C_{14}H_{30}$	7.719	820.1
C_7H_{16}	6.288	513.6	$C_{15}H_{32}$	7.884	840.2
C_8H_{18}	6.311	629.8	$C_{16}H_{34}$	8.064	869.9

Some remarks

Using molecular dynamics simulations, the diffusion coefficients of various classes of polyatomic molecules were determined in the temperature range 500K – 1000K. The effects of molecular structure on diffusion were quantified using the radius of gyration of the molecules. The importance of this research I highlighted in the computational study reported below.

Using the CHEMKIN suite of programs, the new transport data were implemented in at flame code to determine the strain rate of flames of dodecane. The figure below shows a comparison between the results obtained with MD versus C-E theory, demonstrating a significant discrepancy between the two approaches.



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