Real Gas Model Parameters for High-Density Combustion from Chemical Kinetic Model Data

Chenwei Zheng, Deshawn Murray Coombs, and Benjamin Akih-Kumgeh*

Department of Mechanical and Aerospace Engineering, Syracuse University, Syracuse, New York 13210, United States

ABSTRACT: Low emissions and high efficiencies can be realized in combustion systems that operate at high-pressure and low-temperature conditions (high densities). The design of such engines relies on accurate models of the physical processes involved. Under these conditions, the ideal gas model widely used in computational fluid dynamics (CFD) simulations fails to properly capture the relation among pressure, density, and temperature as well as inter-relations among other thermodynamic and transport properties. As such, discrepancies between experimental observations and CFD simulations cannot only be traced to uncertainties from experiments, turbulent, or combustion models. This paper offers a possible solution to the implementation of the real gas equation of state models in combustion simulations. The large number of species in combustion simulations requires effort to provide the relevant real gas properties. A method is suggested for incorporating these properties in simulations based on available transport and thermodynamic data of chemical kinetic models. This attempt also brings out an often-ignored problem in existing chemical kinetic models in the literature, namely, the nonsystematic assignment of transport properties for various species. To clearly demonstrate the need for real gas models in reacting flows, simulations are carried out of a high-pressure n-heptane jet into a quiescent chamber of air based on ideal gas and real gas models. The defects of the ideal gas model are revealed, and the proposed method of property estimation is justified as a convenient solution.

1. INTRODUCTION

Advanced combustion systems characterized by high efficiencies and low emissions can be realized by organizing combustion processes at high pressures and low or moderate temperature conditions. For example, modern diesel engines with turbo chargers reach pressures at about 100 atm; gas turbines now approach 50 atm at take off; and rocket engines operate around 200–300 atm. Combustion systems under these conditions require real gas models.

The need to account for real gas effects in computational fluid dynamics (CFD) simulations has been recognized, with the result that increasingly more studies try to address this problem.1-10 Recent comprehensive reviews of work on real gas behavior in reacting flows have been presented by Bellan11 Sazhin12 and Yang.13 These works established that the fluid flow is different once either pressure or temperature exceeds the critical state values. In addition to all of the classical problems of multiphase chemically reacting flows, a unique set of problem arises from the introduction of thermodynamic nonidealities and transport anomalies. Models of real gas behavior are needed.

There are many models of real gas equations of state used in CFD. These include theoretically grounded equations, such as the van der Waals equation. Complex empirical equations of state are also used, including the 32-term version of the Benedict–Webb–Rubin (BWR) equation.14,15 Most practical real gas equation of state (EOS) is modifications of the semi-empirical van der Waals EOS. Currently, in order to simplify computational tasks associated with EOS evaluations, two-term cubic equations of state such as the Redlich–Kwong (RK) model,16 Soave–Redlich–Kwong (SRK),17 and Peng–Robinson (PR)18 are widely used for research projects. These models should also bridge the vapor and liquid states.

Vapor–liquid equilibrium processes of n-alkanes from C3 to C20 were presented by Zhu and Reitz19 to examine the effects in nonreacting flows, simulations can be described in mixing problems. In this area, Yang’s group20,21 and Bellan’s research group22,23 have carried out several simulation studies. Oefelein and Yang24 used large eddy simulation (LES) to study the 2D mixing of hydrogen and oxygen. Choices for real gas behavior were the 32-term BWR EOS14 proposed by Jacobsen and Stewart25 near critical points and the SRK real gas model elsewhere.25 Bellan’s team22,23 opted for the PR EOS in direct numerical simulation and the LES study of high-pressure mixing layers.

Apart from nonreacting flows, real gas effects have been included in several reacting flow simulations with simplified chemistry models.26-33 The consideration of real gas effects

Received: November 12, 2018
Accepted: February 1, 2019
Published: February 12, 2019
resulted in the change of the flow structure and development of the flow. Kim et al.30 simulated a liquid rocket reacting flow, where liquid oxygen (83 K) and gaseous hydrogen (275 K) were introduced to a combustion chamber at 6.0 MPa. The simulation used a modified SRK EOS and consistent thermodynamics along with a real fluid flamelet model, formulated in a mixture fraction space. The real-fluid flamelet was found to be capable of realistically predicting the overall characteristics of a turbulent nonpremixed GH2/LOx flame at supercritical pressures.

With the need to include more chemical kinetic effects in combustion simulations, one encounters a high number of species whose critical properties are not well known or would be too cumbersome to be assigned manually. It is preferable that any method used to address this problem be computationally convenient.

This paper develops a framework to generate parameters of real gas EOS from transport and thermodynamics data, which are available and are already used in combustion chemical kinetic models.34 We first describe the method to obtain required real gas EOS parameters from chemical kinetic models and their associated data.35,36 We further highlight an existing problem in the way current transport data are estimated because significant differences are observed. Thereafter, we demonstrate through simulations that using real gas EOS leads to differences in the flow field at combustion-relevant conditions, compared to simulations based on ideal gas EOS. As further justification for the proposed solution, we review the theoretical link between EOS parameters and transport properties, namely, their relation to intermolecular potentials.

2. RESULTS AND DISCUSSION

2.1. Method of EOS Parameter Estimation. Our goal is to determine for each species in a given mechanism its real gas EOS parameters, that is, \( T_c, P_c, \text{ and } \omega \). Using an appropriate mixing rule, the EOS parameters for a given combustion gas mixture can be determined from those of the individual species. As mentioned before, for reacting flow simulation, there is a connection between the critical state properties and the parameters of intermolecular potentials. The latter are used in combustion flows to generate required transport properties (viscosity, conductivity, and thermal diffusivity). One can reverse-engineer the transport data to obtain the critical gas EOS and the parameters of intermolecular potentials. The latter are used in combustion flows to generate required transport properties (viscosity, conductivity, and thermal diffusivity). One can

\[
\sigma \left( \frac{P}{T_c} \right)^{1/3} = a_\sigma - b_\sigma \omega \\
\varepsilon = a_\varepsilon - b_\varepsilon \omega
\]

where \( \varepsilon \) is the depth of the potential well and \( \sigma \) is the distance at which the potential is zero.

In chemical kinetic models, the estimation rules proposed in Kee et al.38 are often used. It appears that the Kee et al.37 performed better than the Kee et al.38 when predicted transport variables are compared with empirical observations.

### Table 1. Parameters for Estimation

| Methods    | Tee et al.37 | Kee et al.38 | Holley et al.39 |
|------------|--------------|--------------|-----------------|
| \( a_\sigma \) | 2.3551       | 2.393        | 2.5551          |
| \( b_\sigma \) | 0.0874       | 0            | 0.3955          |
| \( a_\varepsilon \) | 0.7915       | 0.75         | 0.8063          |
| \( b_\varepsilon \) | 0.1693       | 0            | 0.6802          |

\( T_c, P_c, \text{ and } \omega \) are observable or experimentally derivable quantities whereas the accuracy of \( \sigma \) and \( \varepsilon \) can only be inferred from their prediction of transport properties. This circularity can lead to a verification problem. Holley et al.39 have suggested updated coefficients for the Tee correlation. This means that with an appropriate correlation, one can obtain \( T_c \) and \( P_c \) from transport data, as far as consistency in applied estimating \( \sigma, \varepsilon \) from properties, and reverse calculation of those properties from \( \sigma, \varepsilon \).

The acentric factor, \( \omega \), poses a challenge that can only be resolved through structure–activity correlations. For instance, for alkanes, it can be established that \( \omega \) depends on the number of carbon (\( N_c \)): \( \omega = 0.0004423 [\ln (3.3063 + 3.4381 N_c)]^{2.3551} \). The necessary carbon number can be obtained from the model thermodynamic data file. Taken together, the above offers ways to generate critical state properties and hence EOS parameters from currently available resources.

One might check the effectiveness of the proposed approach by comparing predicted critical state parameters with measured data for some species of relevance to combustion. An example is shown in Figure 1 for C1–C12 n-alkanes with critical properties from the literature.25 Intermolecular potential parameters \( \sigma \) and \( \varepsilon \) are chosen from the JetSurf 2.0 mechanism36 and LLNL n-heptane mechanism, respectively. The observed differences in \( T_c \) and \( P_c \) are quite small, and there are often not given critical attention in model evaluations.

As shown in Figure 1, Tee’s correlation with the LLNL chemical kinetic database provides accurate critical properties. While for large carbon alkanes, Holley’s correlation with JetSurf 2.0 shows good agreement with experimental data, for small carbon alkanes, the correlation results in inconsistency. Kee’s correlation does not require an acentric factor but errors occur as the carbon number increases because of deviation from the spherical shape. Therefore, we recommend using Tee’s correlation with the LLNL database. This correlation can still be used with other databases. The methodical differences are still insignificant compared to using the ideal gas model at high-density conditions.

2.2. Algorithmic Description of Implementing the Method. Steps to using chemical kinetic files for CFD simulation (Figure 2):

1. Identify species in the model and locate the transport data
2. Locate the thermochemical file carbon number and estimate the acentric factor \( \omega \)
3. Use appropriate correlation to determine \( T_c \) and \( P_c \)
4. Determine the EOS properties \( a_\sigma \) and \( b_\sigma \) for each species
5. Save \( T_c, P_c, \omega, a_\sigma, b_\sigma \) to a file
6. During computation, read in \( T_c, P_c, \omega, a_\sigma, b_\sigma \) and file to apply the mixing rule to code

2.3. LES of n-Heptane Jets. The problem we consider here consists of an n-heptane jet introduced into a hot chamber of air to investigate the effect of real gas models on CFD simulations of mixing. Two different types of inlet
conditions, which are kept constant for simulations, are used. In the first case, we keep the inlet velocity of 86 m/s using both ideal gas EOS and real gas EOS. In the second case, the momentum is the same, thus, when the ideal gas EOS velocity is 86 m/s, the real gas velocity is reduced to 53.73 m/s to obtain the same momentum because of the density difference.

The conditions are such that the chamber filled with air at 50 atm has a temperature of 1050 K. The subsonic n-heptane jet is injected with a temperature of $T = 575$ K. Simulations are carried out using both ideal gas EOS and real gas (PR) EOS for species. The real gas EOS requires the critical state parameters and acentric factor, which for n-heptane are $T_c = 540.15$ K, $P_c = 27.36$ bar, and $\omega = 0.349$; for oxygen are $T_c = 154.58$ K, $P_c = 50.43$ bar, and $\omega = 0.025$; and for nitrogen are $T_c = 126.20$ K, $P_c = 34.00$ bar, and $\omega = 0.039$.

In order to properly resolve the flow field, the turbulence model chosen here is LES with wall-adapting local eddy as the subgrid scale model. To simulate the combustion flow field, the eddy-break up model is employed. The mesh consists of 2 393 042 cells in total with a minimum cell size $\Delta x_{\text{min}} = 0.1$ mm. Simulation is carried out using the segregated solver of Star-CCM+. The time discretization is implicit, and to obtain good convergence of the solver at each time step, the following under-relaxation factors were used, 0.8 for velocity, 0.2 for

Figure 1. Critical property estimation based on intermolecular constants. (a,b) are estimated $T_c$ and $P_c$ based on Tee’s method; (c,d) are estimated $T_c$ and $P_c$ based on Kee’s method; (e,f) are estimated $T_c$ and $P_c$ based on Holley’s method.

Figure 2. Algorithmic description flow chart.

Figure 3. Nonreacting temperature contour at 0.5 and 1.0 ms. Top: ideal gas; bottom: real gas.
pressure, and 0.9 for both the species and energy equations. A maximum of 50 iterations for the iterative matrix solvers was used to ensure the solution reached a converged state at each time step. The time step was set to a maximum local CFL number of approximately 2.4.

2.3.1. Case 1: Inlet Speed the Same. The resulting flow field can be compared using scalars such as the temperature and Q-criterion as a measure of vorticity. Figure 3 is the instantaneous temperature profile with a nonreacting flow. The spread and penetration depth of the flow are different between ideal gas and real gas with PR EOS, predicting a further propagated flow. Similar flow pattern could be found in the reacting case, as shown in Figure 4. With the combustion model, the flow contains higher energy, hence, the difference is more pronounced. The temperature fields also reflect differences that align with the mixing field. These fields are affected through the use of the EOS to relate the pressure, density, and temperature, which appear in the conservation equations.

Instantaneous snapshots of the jet dynamics at two different instances in time are shown in Figure 5 through isosurfaces of the Q-criterion colored with temperature. The Q-criterion is an appropriate quantity to visualize coherent structures from LES. Coherent structures in the form of horseshoe vortices are visible at the edge of the jet. These structures contain a major

Figure 4. Temperature contour at 0.5 and 1.0 ms for a combustion flow of n-heptane showing effect of EOS. Top: ideal gas; bottom: real gas.

Figure 5. Q-Criterion isosurface ($Q = 5 \times 10^8$). (a,b) Ideal gas model, (c,d) real gas model; nonreacting results are on the top and reacting results are at the bottom. Colored by temperature in [K] at 1 ms.
fraction of the energy. As a result of the lower chemistry of the ideal gas, low momentum is injected into the flow compared to the case of the real gas. This leads to lower energy content and faster dissipation of coherent structures in ideal gas.

Similar behavior is observed between nonreacting and reacting flow, where the combustion model generates more turbulent energy and coupled with the higher momentum, the real gas case reaches to a stronger coherent structure.

These differences have implications on the interpretation of experimental data used for validation. It must be justified whether the inlet conditions are estimated based on assumption of a given EOS.

2.3.2. Case 2: Flow-Field Comparison for the Same Inlet Mass Flow Rate. From Figure 4, we see that the choice of EOS in the simulation of high-pressure combustion systems, such a fuel injection is important to the prediction of the flow field. Using a constant velocity boundary condition with the real gas and ideal gas EOS models results in difference in the penetration depth, with the real gas jet going further. This occurs because of the differences in the inlet momentum of the two jets. An interesting question would be to see whether the penetration depth be made similar by prescribing the same momentum for the two cases. This would validate the explanation for the differences in Figure 4.

In Figures 6 and 7, we compare the results from real gas and ideal gas EOS simulations in which the inlet jet mass flow rate is held fixed at 0.1 kg/s. Because of the higher density of the real gas EOS prediction, the inlet velocity is low, requiring more time to reach the same penetration depth.

2.3.3. Case 3: Flow-Field Comparison for the Same Inlet Momentum. From Figure 4, we see that the choice of EOS in the simulation of high-pressure combustion systems, such a fuel injection is important to the prediction of the flow field. Using a constant velocity boundary condition with the real gas and ideal gas EOS models results in difference in the penetration depth, with the real gas jet going further. This occurs because of the differences in the inlet momentum of the two jets. An interesting question would be to see whether the

penetration depth be made similar by prescribing the same momentum for the two cases. This would validate the explanation for the differences in Figure 4.

In Figures 8 and 9, we compare the results from real gas and ideal gas EOS simulations in which the inlet jet momentum is held fixed. Because of the higher density of the real gas EOS prediction, the inlet velocity is low, requiring more time to reach the same penetration depth.

The above discussion brings to light another problem that must be considered in the simulation of physical problems or experiments, the errors that can occur due to boundary conditions. For experiments of fuel injection, the injection boundary conditions would be specified either as a measured mass flow rate or a velocity. The boundary condition would then be interpreted by the numerical modeler and adjusted to velocity or the mass flow rate to fit with the numerical model of the experiment. In a high-pressure combustion simulation,
the careful interpretation of these boundary conditions and the EOS assumptions that have been made during the measurement is important to the comparison of experiment and computation.

The observed differences in the flow field thus justify the need for real gas models. The method of estimating these real gas model parameters from available resources is a convenient solution.

3. CONCLUSIONS

In this paper, the problem of real gas equations of state for high-density flow simulations is considered. The importance of such equations of state is underlined by comparing the LES results of an \( n \)-heptane jet into an air vessel realized using LES with ideal and real gas equations of state. It is then suggested that parameters of a cubic EOS, namely, the critical state variables, can be determined from the transport data of chemical kinetic models. It is further observed that the transport data of various chemical kinetic models are not necessarily consistent, suggesting further attention to this modeling problem.

4. COMPUTATIONAL METHODS

This paper presents a solution to real gas model parameter estimations. This section sketches the theoretical background to the estimation approach. It first shows how real gas effects enter into CFD simulation. It then discusses EOS models and intermolecular potentials.

4.1. Real Gas Effects in CFD Modeling and Analysis.

Accurate determination of density and other thermodynamic properties based on the EOS is very important because CFD governing equations are sensitive to these. The index notation form of the governing equations for chemically reacting flows is

\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} = 0
\]

(3)

\[
\frac{\partial (\rho u_i)}{\partial t} + \frac{\partial (\rho u_i u_j)}{\partial x_j} = \frac{\partial \sigma_{ij}}{\partial x_j} \quad (i = 1,2,3)
\]

(4)

\[
\frac{\partial (\rho E)}{\partial t} + \frac{\partial (\rho (E + p) u_i)}{\partial x_i} = \frac{\partial q_i}{\partial x_i} + \frac{\partial (u_i \tau_{ij})}{\partial x_j}
\]

(5)

\[
\frac{\partial (\rho Y_j)}{\partial t} + \frac{\partial (\rho Y_j u_i)}{\partial x_i} = \dot{\omega}_k + \frac{\partial (\rho D_{ij} \dot{Y}_j)}{\partial x_j}
\]

(6)

The density deviation of the ideal gas law cannot be ignored at high-density conditions because it can be large as shown in Figure 10. The ideal gas law deviation of density increases when the carbon number becomes larger, while the real gas equations of state provide good agreements with experimental data. PR and RK seem to do comparably well over a range of conditions. When it comes to large hydrocarbon fuels, the SRK seems to be preferred. The PR and RK can be recommended, unless special considerations demand use of more complex RG EOS.

Thermodynamic properties are generally taken as the sum of values provided by the ideal gas model and a departure function accounting for the real gas effects. The difference in flow patterns can be induced by the departure function in internal energy or enthalpy

\[
du = C_v dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv
\]

(7)

Figure 9. Q-criterion isosurface (\( Q = 5 \times 10^5 \)). Colored by temperature in [K] at 1 ms. Reacting experiment with the fixed momentum inlet condition. Top: ideal gas; bottom: real gas.

Figure 10. Variation of \( n \)-propane and \( n \)-heptane density with temperature (at \( P = 50 \) atm), highlighting importance of real gas EOS.

(a) \( n-C_3H_8 \), \( T - \rho \) variation. (b) \( n-C_7H_{16} \), \( T - \rho \) variation.
\[ dh = C_p \, dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right) \right]_u \, dP \]

where the second terms are the departure terms. While the ideal gas EOS will result in zero for the departure term, real gas EOS contributes to the overall function. Therefore, the energy function would be slightly different for the two EOS, and eventually causing the variation in the flow field.

### 4.2. Modeling Real Gas EOS

Semiempirical cubic equations of state for real gases are used widely in combustion simulation projects because of their simplicity. For a pure compound, the cubic EOS requires critical properties, \( T_c \) and \( P_c \), as input, while some of the equations need the acentric factor, \( \omega \). By applying certain mixing rules, one can obtain the EOS parameters for the multicomponent mixture.

According to Zhu and Reitz,\(^{19}\) the general form of cubic equations of state can be written as

\[ p = \frac{RT}{V - b} - \frac{a}{V^2 + qbV + wb^2} \]

where \( V \) is the volume of a system and \( R \) is the universal gas constant; \( a \) and \( w \) are constants depending on the type of cubic EOS. For pure species, \( a \) and \( b \) are functions of temperature. The expressions for EOS parameters are presented in Table 2.

### Table 2. Parameters for Cubic EOS

| Equation name | \( b \) | \( a \) | \( q \) | \( w \) |
|---------------|--------|--------|--------|--------|
| RK \( \frac{0.086RT_c}{P_c} \) | 0.04278RT_c^{1.25} | 1 | 0 |
| SRK \( \frac{0.08664RT_c}{P_c} \) | 0.42747RT_c^{1.25} \( [1 + \kappa(1 - T_c^{2.5})]^2 \) | 1 | 0 |
| PR \( \frac{0.07780RT_c}{P_c} \) | 0.45724RT_c^{1.25} \( [1 + \kappa(1 - T_c^{2.5})]^2 \) | 2 | -1 |

where \( T_c \) and \( P_c \) are critical temperature and critical pressure, \( \omega \) is the acentric factor, and \( \kappa \) is a constant that depends on the acentric factor and the reduced temperature, \( T_r = T/T_c \).

For multicomponent systems, a binary mixing rule with regard to \( a \) and \( b \) is suggested by Peng and Robinson\(^{18}\) as

\[ a = \sum_i \sum_{i<j} x_i x_j a_{ij} \]

\[ b = \sum_i x_i b_i \]

\[ a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2} \]

where \( \delta_{ij} \) is an empirically determined binary interaction coefficient, characterizing the binary interaction formed by component \( i \) and component \( j \). \( \delta_{ij} \) is observed to lie between \(-0.2 \) and \( 0.2 \) and in majority binary mixtures, it is postulated to be \( 0.0 \).\(^{31}\)

Another method to deal with the mixing rule is the pseudocritical method based on the corresponding state principle (CSP). To obtain an EOS, we first calculate the pseudocritical properties for the mixture. According to Poling et al.\(^{25}\) the pseudocritical temperature \( T_{cm} \) can be estimated by the simplest mole fraction average method:\(^{42}\) \( T_{cm} = \sum_i y_i T_{ci} \).

As for the pseudocritical pressure, \( P_{cm} \), a mole fraction average of pure-component critical pressures is normally unsatisfactory. This is because the critical pressure for most systems goes through a maximum or minimum with composition. The only exceptions are if all components of the mixture have similar critical pressures or critical volumes. The simplest rule which can give acceptable \( P_{cm} \) values for two-parameter or three-parameter CSP is the modified rule of Pratsnitz and Gunn\(^{43}\)

\[ P_{cm} = \frac{Z_{cm} RT_{cm}}{V_{cm}} = \left( \frac{\sum_{i=1}^n y_i z_i}{\sum_{i=1}^n y_i T_i} \right) \]

where all of the mixture pseudocriticals \( Z_{cm}, T_{cm}, \) and \( V_{cm} \) are given by mole fraction averages and \( R \) is the universal gas constant.

The mixture pseudoacentric factor is commonly given by a mole fraction average\(^{44}\)

\[ \omega_{cm} = \sum_{i=1}^n y_i \omega_i \]

Thus, with knowledge of the critical temperature and critical pressure of each species, the EOS for the mixture is determined.

### 4.3. Intermolecular Potentials and Combustion Modeling

For ideal gases, it is usual to assume elastic collision to be such that no interacting forces are felt beyond a characteristic separation \( r > \sigma \), but the potential is infinite for \( r \leq \sigma \), necessitating bounce off. Ideal gases hold that most of the time, gaseous particles are sufficiently far apart such that no forces are felt except during collision. The situation changes in dense fluids.

In real fluids, particles interact with others according to an intermolecular potential which is a superposition of nuclei-electrons attraction and electrons-electrons or nuclei-nuclei repulsion. Various modeling approaches exist for describing the potential in interacting systems, from the simplest model rigid impenetrable spheres to complicated four-parameter Buckingham potential. The most widely used Lennard-Jones 6-12 potential is defined as\(^{45}\)

\[ \phi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

where \( \varepsilon \) is the potential energy depth, and \( \sigma \) is the distance at which the interparticle potential is zero. These parameters are illustrated in Figure 11.

In combustion simulations involving chemical kinetic models, Lennard-Jones potential parameters are widely used to determine transport properties, such as the viscosity, thermal conductivity, and diffusion coefficient, because these transport processes are grounded in the momentum exchange of particles.\(^{34}\)

The viscosity of a simple coefficient is given by\(^{47}\)

\[ \mu_i = 5 \frac{\sqrt{\pi m_i k_b T}}{16 \pi n_i^2 \Omega_i^{2.5}} \]

where \( m_i \) is the molecular mass, \( k_b \) is the Boltzmann constant, \( T \) is the temperature, and \( \Omega_i \) is the Lennard-Jones collision diameter.

The thermal conductivity can be obtained from
\[ \lambda_i = A C_{ij} \mu_i \]  

where \( A \) is a constant and \( C_{ij} \) is the specific heat capacity at constant volume for species \( i \).

The binary diffusion coefficient for species \( i \) and \( j \) is defined as

\[ D_{ij} = \frac{3}{16} \frac{2\pi k_B^2 \sigma^3}{m_{ij} \rho_{ij}} \]

\( \sigma^{1.6} \) and \( \Omega^{2.26} \) are dimensionless collision integrals as a function of \( T_b^* = \frac{k_B T}{\rho} \), which have been provided by Monchick and Mason.  

Thus, with knowledge of \( \sigma \) and \( \epsilon \) of each species, the transport properties are fully determined.

4.4. Real Gas EOS and Lennard-Jones Potential. The widely used two-term cubic equations of state such as the RK model, (SRK) and PR require the critical properties of chemical species.

The critical and phase change properties of a fluid reflect the nature of intermolecular interactions. A direct theoretical connection or correlation has been sought to link critical state parameters to molecular dynamics. Therefore, real gas properties have been investigated by many groups using molecular dynamics and Monte Carlo simulations, starting with Wood and Parker. Verlet later used the Lennard-Jones potential to study the EOS of a fluid. Subsequently, an accurate EOS database was compiled by Nicolas et al. After many more studies, the EOS was refitted by Johnson et al. Frenkel and Smit used the Monte Carlo simulation to predict the results from Johnson et al., including the vapor–liquid coexistence region. Traditionally, the Lennard-Jones potential is used to model hard-core neutral atoms or spherical molecules. With the development of the statistical-associated fluid theory, the Lennard-Jones EOS was analytically studied for hard-core homo-nuclear chain molecules. extended the theory into pure and binary \( n \)-alkane systems and presented an accurate estimation of phase equilibrium.

With accurate description of the molecular interactions, it is therefore possible to predict real gas behavior. The connection between Lennard-Jones potentials of spherical molecules and their critical properties can be explored using Monte Carlo simulations. However for more practical applications, semi-empirical relations are needed for rapid estimation of state properties from molecular potential parameters.

For each species in a given chemical kinetic model, its real gas EOS parameters, that is, \( T_c, P_c, \omega \), can therefore be estimated. Using an appropriate mixing rule, the EOS parameters for a given combustion gas mixture can then be determined from those of the individual species. As mentioned before, for reacting flow simulation, there is a connection between the critical state properties and the parameters of intermolecular potentials. The latter are used in combustion flows to generate required transport properties (viscosity, conductivity, and thermal diffusivity). One can therefore reverse-engineer the transport data to obtain the critical state parameters needed for the EOS, as done in Section 2.

## Author Information

**Corresponding Author**

*E-mail: bakihkum@syr.edu.*

**ORCID**

Benjamin Akih-Kumgeh: 0000-0001-5305-1977

**Notes**

The authors declare no competing financial interest.

## Acknowledgments

C.Z. was supported by Syracuse University Water Fellowship and NRT: Education Model Program on Water-Energy Research (EMPOWER) at Syracuse University (DGE-1449617). This research was supported in part through computational resources provided by Syracuse University.

## References

1. Williams, A. Combustion of droplets of liquid fuels: a review. *Combust. Flame* 1973, 21, 1–31.

2. Reitz, R.; Rutland, C. Development and testing of diesel engine CFD models. *Prog. Energy Combust. Sci.* 1995, 21, 173–196.

3. Aggarwal, S. K. A review of spray ignition phenomena: present status and future research. *Prog. Energy Combust. Sci.* 1998, 24, 565–600.

4. Müller, R. S.; Harstad, K. G.; Bellan, J. Direct numerical simulations of supercritical fluid mixing layers applied to heptane–nitrogen. *J. Fluid Mech.* 2001, 436, 1–39.

5. Schmitt, T.; Selle, L.; Cuenot, B.; Poinot, T. Large-Eddy Simulation of transcritical flows. *Comptes Rendus Mec.* 2009, 337, 528–538.

6. Schmitt, T.; Selle, L.; Ruiz, A.; Cuenot, B. Large-eddy simulation of supercritical-pressure round jets. *AIAA J.* 2010, 48, 2133–2144.

7. Jarczyk, M.-M.; Pfützner, M. Large eddy simulation of supercritical nitrogen jets. 50th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, 2012; p 1270.

8. Müller, H.; Niedermeier, C. A.; Jarczyk, M.; Pfützner, M.; Hickel, S.; Adams, N. A. Large-eddy simulation of trans-and supercritical injection. *Progress in Propulsion Physics*, 2016; Vol. 8, pp 5–24.

9. Hempert, F.; Boblest, S.; Ertl, T.; Sadlo, F.; Offenhäuser, P.; Glass, C. W.C.; Hoffmann, M.; Beck, A.; Munz, C.-D.; Iben, U. Simulation of real gas effects in supersonic methane jets using a tabulated equation of state with a discontinuous Galerkin spectral element method. *Comput. Fluids* 2017, 145, 167–179.

10. Zheng, C.; Coombs, D.; Akih-Kumgeh, B. Modelling Real Gas Equations of State in High Density Combustion; ICDERS: Boston, USA, July 30–Aug 4, 2017.

11. Bellan, J. Supercritical (and subcritical) fluid behavior and modeling: drops, streams, shear and mixing layers, jets and sprays. *Prog. Energy Combust. Sci.* 2000, 26, 326.
(12) Sazhin, S. Advanced models of fuel droplet heating and evaporation. Prog. Combust. Sci. 2006, 32, 162.
(13) Yang, V. Modeling of supercritical vaporization, mixing, and combustion processes in liquid-fueled propulsion systems. Proc. Combust. Inst. 2000, 28, 925.
(14) Benedict, M.; Webb, G. B.; Rubin, L. C. An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures II. Mixtures of Methane, Ethane, Propane, and n-Butane. J. Chem. Phys. 1942, 10, 747–758.
(15) Younglove, B. A.; Ely, J. F. Thermophysical properties of fluids. II. Methane, ethane, propane, isobutane, and normal butane. J. Phys. Chem. Ref. Data 1987, 16, 577–798.
(16) Redlich, O.; Kwong, J. N. S. On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. Chem. Rev. 1949, 44, 233–244.
(17) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. Chem. Eng. Sci. 1972, 27, 1197–1203.
(18) Peng, D.-Y.; Robinson, D. B. A new two-constant equation of state. Ind. Eng. Chem. Fundam. 1976, 15, 59–64.
(19) Zhu, G.-S.; Reitz, R. D. A model for high-pressure vaporization of droplets of complex liquid mixtures using continuous thermodynamics. Int. J. Heat Mass Transfer 2002, 45, 495.
(20) Oefeine, J. C.; Yang, V. Modeling high-pressure mixing and combustion processes in liquid rocket engines. J. Propul. Power 1998, 14, 843.
(21) Zong, N.; Meng, H.; Hsieh, S.-Y.; Yang, V. A numerical study of cryogenic fluid injection and mixing under supercritical conditions. Phys. Fluids 2004, 16, 4248–4261.
(22) Okong’o, N.; Bellan, J. Perturbation and initial Reynolds number effects on transition attainment of supercritical, binary, temporal mixing layers. Comput. Fluids 2004, 33, 1023–1046.
(23) Taskinoglu, E. S.; Bellan, J. A posteriori study using a DNS database describing fluid disintegration and binary-species mixing under supercritical pressure: heptane and nitrogen. J. Fluid Mech. 2010, 645, 211–254.
(24) Jacobsen, R. T.; Stewart, R. B. Thermodynamic properties of nitrogen including liquid and vapor phases from 63K to 2000K with pressures to 10,000 bar. J. Phys. Chem. Ref. Data 1973, 2, 757–922.
(25) Poling, B. E.; Prausnitz, J. M.; O’connell, J. P. The properties of gases and liquids; McGraw-hill: New York, 2001; Vol. 5.
(26) Oefeine, J. C. Mixing and combustion of cryogenic oxygen-hydrogen shear-coaxial jet flames at supercritical pressure. Combust. Sci. Technol. 2006, 178, 229–252.
(27) Zong, N.; Yang, V. Near-field flow and flame dynamics of LOX/methane shear-coaxial injector under supercritical conditions. Proc. Combust. Inst. 2007, 31, 2309–2317.
(28) Schmitt, T.; Méry, Y.; Boileau, M.; Candel, S. Large-eddy simulation of oxygen/methane flames under transcritical conditions. Proc. Combust. Inst. 2011, 33, 1383–1390.
(29) Matsuyama, S.; Shinjo, J.; Ogawa, S.; Mizobuchi, Y. Large eddy simulation of LOX/GH2 shear-coaxial jet flame at supercritical pressure. 48th AIAA Aerospace Sciences Meeting Including The New Horizons Forum and Exposition 2010; p 208.
(30) Kim, T.; Kim, Y.; Kim, S.-K. Real-fluid flamelet modeling for gaseous hydrogen/cryogenic liquid oxygen jet flames at supercritical pressure. J. Supercri. Fluids 2011, 58, 254–262.
(31) Pohl, S.; Jarzczek, M.; Pitzner, M.; Rögg, B. Real gas CFD simulations of hydrogen/oxygen supercritical combustion. Progress in Propulsion Physics, 2013; Vol. 4, pp 583–614.
(32) Huo, H.; Yang, V. Large-Eddy Simulation of Supercritical Combustion: Model Validation Against Gaseous H2-O2 Injector. J. Propul. Power 2017, 33, 1272–1284.
(33) Bellan, J. Evaluation of mixture-fraction-based turbulent-reaction-rate model assumptions for high-pressure reactive flows. Combust Flame 2017, 179, 253–266.
(34) Kee, R. J.; Dixon-Lewis, G.; Warnatz, J.; Coltrin, M. E.; Miller, J. A. A Fortran Computer Code Package For The Evaluation Of Gas-Phase Multicomponent Transport Properties; Sandia National Laboratories; Report SAND86-8246, 1986; Vol. 13, pp 80401–81887.
(35) Mehhl, M.; Pitz, W. J.; Westbrook, C. K.; Curran, H. J. Kinetic modeling of gasoline surrogate components and mixtures under engine conditions. Proc. Combust. Inst. 2011, 33, 193–200.
(36) Wang, H.; Dames, E.; Sirjean, B.; Sheen, D.; Tangko, R.; Violi, A.; Lai, J.; Egoldopoulos, F.; Davidson, D.; Hanson, R.; Bowman, C. A high-temperature chemical kinetic model of n-alkane (up to n-docosane), cyclohexane, and methyl, ethyl, n-propyl and n-butyl-cyclohexane oxidation at high temperatures. JetSurf, version 2.0, 2010; Vol. 2; p 19.
(37) Tee, L. S.; Gotoh, S.; Stewart, W. E. Molecular parameters for normal fluids. Lennard-Jones 12-6 Potential. Ind. Eng. Chem. Fundam. 1966, 5, 356–363.
(38) Kee, R.; Coltrin, M.; Glarborg, P. Chemically Reacting Flow: Theory and Practice; John Wiley & Sons, 2005.
(39) Holley, A. T.; You, X. Q.; Dames, E.; Wang, H.; Egoldopoulos, F. N. Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion. Proc. Combust. Inst. 2009, 32, 1157.
(40) Han, B.; Peng, D.-Y. A groupcontribution correlation for predicting the acentric factors of organic compounds. Can. J. Chem. 1993, 71, 332.
(41) Aboudour, A. M.; Mohammad, S. A.; Robinson, R. L., Jr.; Gasem, K. A. M. Generalized binary interaction parameters for the Peng-Robinson equation of state. Fluid Phase Equilib. 2014, 383, 156–173.
(42) Kay, W. B. Gases and vapors at high temperature and pressure-density of hydrocarbon. Ind. Eng. Chem. 1936, 28, 1014–1019.
(43) Prausnitz, J. M.; Gann, R. D. Volumetric properties of nonpolar gaseous mixtures. AIChE J. 1958, 4, 430–435.
(44) Joffe, J. Combining rules for the third parameter in the pseudoclassical method for mixtures. Ind. Eng. Chem. Fundam. 1971, 10, 532–533.
(45) Laurendeau, N. M. Statistical Thermodynamics: Fundamentals and Applications; Cambridge University Press, 2005.
(46) Jiang, C. Y. A. New Approach to Model Adsorption in Heterogeneous Phase System with Monte Carlo Method. Am. J. Mater. Sci. 2014, 4, 25–38.
(47) Hirschfelder, J.; Bird, R. B.; Curtiss, C. F. Molecular Theory of Gases and Liquids; Wiley, 1964.
(48) Warnatz, J. Numerical Methods In Laminar Flame Propagation; Springer, 1982; pp 87–111.
(49) Monchich, L.; Mason, E. A. Transport properties of polar gases. J. Chem. Phys. 1961, 35, 1676–1697.
(50) Wood, W. W.; Parker, F. R. Monte Carlo Equation of State of Molecules Interacting with the Lennard-Jones Potential. I. A Supercritical Isotherm at about Twice the Critical Temperature. J. Chem. Phys. 1957, 27, 720–733.
(51) Verlet, L. Computer “Experiments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. Phys. Rev. 1967, 159, 98.
(52) Nicolas, J. J.; Gubbins, K. E.; Streett, W. B.; Tildenley, D. J. Equation of state for the Lennard-Jones fluid. Mol. Phys. 1979, 42, 1429–1454.
(53) Johnson, J. K.; Zollweg, J. A.; Gubbins, K. E. The Lennard-Jones equation of state revisited. Mol. Phys. 1993, 78, 591–618.
(54) Frenkel, D.; Smit, B. Understanding Molecular Simulation: From First Principles to Applications; Elsevier (formerly published by Academic Press), 2002; Vol. 1.
(55) Wertheim, M. S. Thermodynamic perturbation theory of polymerization. J. Chem. Phys. 1987, 87, 7333–7331.
(56) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New reference equation of state for associating liquids. Ind. Eng. Chem. Res. 1990, 29, 1709–1721.
(57) Chiew, Y. C. Percus-Yevick integral-equation theory for athermal hard-sphere chains. Mol. Phys. 1990, 70, 129–143.
(58) Chen, C.-k.; Banaszak, M.; Radosz, M. Statistical Associating Fluid Theory Equation of State with Lennard-Jones Reference Applied to Pure and Binary-Argylkane Systems. J. Phys. Chem. B 1998, 102, 2427–2431.