Liquid jet breakup regimes at supercritical pressures

Rainer N. Dahms^{*} and Joseph C. Oefelein

Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA

Abstract

Previously, a theory has been presented that explains how discrete vapor-liquid interfaces become diminished at certain high-pressure conditions in a manner that leads to well known qualitative trends observed from imaging in a variety of experiments. Rather than surface tension forces, transport processes can dominate over relevant ranges of conditions. In this paper, this framework is now generalized to treat a wide range of fuel-oxidizer combinations in a manner consistent with theories of capillary flows and extended corresponding states theory. Different flow conditions and species-specific molecular properties are shown to produce distinct variations of interfacial structures and local free molecular paths. These variations are shown to occur over the operating ranges in a variety of propulsion and power systems. Despite these variations, the generalized analysis reveals that the envelope of flow conditions at which the transition from classical sprays to diffusion-dominated mixing occurs exhibits a characteristic shape for all liquid-gas combinations. For alkane-oxidizer mixtures, it explains that these conditions shift to higher pressure flow conditions with increasing carbon number and demonstrates that, instead of widely assumed classical spray atomization, diffusion-dominated mixing may occur under relevant high-pressure conditions in many modern devices.

Keywords: Supercritical, Multiphase, Liquid, Injection, Real-Fluid, Breakup Regimes

2010 MSC: 00-01, 99-00

^{*}Corresponding author, Rndahms@sandia.gov, +1 (925) 294 - 6496, P.O. Box 969, MS 9051

1. Introduction

Liquid injection of multicomponent fluids at elevated operating pressures is not well understood. Imaging from a variety of experiments have long shown that under some conditions, when the pressure of the working fluid approaches or exceeds the thermodynamic critical pressure of the liquid phase, the presence of discrete two-phase flow dynamics may become diminished. Then, the characteristic processes of primary and secondary atomization, multicomponent evaporation, and liquid ligament and droplet formation do not occur. As a consequence, the widely acknowledged drop deformation and breakup regimes of two-phase flows [1, 2] do not apply anymore. Instead, the classical gas-liquid interface is replaced by a single-phase diffusion dominated dense-fluid mixing layer, which is substantially affected by non-ideal thermodynamics and transport. Such phenomena have been demonstrated to occur in various systems, such as those that involve the injection of liquid nitrogen or oxygen into environments composed of nitrogen, helium, hydrogen, or argon [3, 4, 5]. Many works have served to corroborate these observations [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36].

Modern theory has long lacked a first-principle explanation for the observed phenomena. In contrast to pure fluids, discrete vapor-liquid interfaces in multicomponent mixtures along with their surface tension forces do not necessarily diminish only because the thermodynamic critical pressure of the liquid phase is exceeded. In recent years, experimental evidence of substantial surface tension forces in various hydrocarbon mixtures at high pressures ($p > 500$ bar) was provided in the literature [37, 38, 39]. It is generally accepted, however, that surface tension forces in multicomponent mixtures diminish once the temperature of the injected liquid phase approaches its critical value. Previous research into gas-liquid interfaces during diesel engine fuel injection processes has shown, however, that those interfaces are generally not heated to their critical temperature due to the lack of enthalpy contained in the unburned ambient gases [40, 41].

30 Recent studies quantified the conditions under which a specific n-dodecane–
nitrogen mixture (relevant for diesel engine fuel injection) transitions between
classical spray atomization and diffusion-dominated dense-fluid mixing dynam-
ics [42, 43, 44]. It was established that the breakdown of the classical non-
continuum two-phase interface and the consequent development of dense-fluid
35 mixing layers is initiated because the multi-component two-phase interface be-
comes much wider than the mean free molecular path. This showed that the
transition to mixing layers occurs due to interfacial dynamics and not, as con-
ventional wisdom had suggested, because the liquid phase has heated to super-
critical temperatures where surface tension forces diminish.

40 The findings outlined above have most recently been corroborated by Manin
et al. [45] by applying long-distance microscopic imaging using an ultra-fast LED
source with a diffuser background behind the n-dodecane jet. When the jet is
injected at lower temperatures but supercritical pressures, classical droplet and
ligament stretch and breakup dynamics were observed. At the high pressure
45 and higher temperature conditions predicted by Dahms *et al.* [42, 43, 44], such
dynamics become diminished and no droplets could be detected anymore. Fur-
thermore, the transition from liquid to gaseous state appeared much smoother
compared to observations made at lower temperature and pressure conditions.
Falgout *et al.* [46] has also provided evidence of dense-fluid mixing layers using
50 ballistic imaging of the same diesel fuel injector at the same chamber condi-
tions. A thickened turbulent n-dodecane–nitrogen mixing layer was found to
evolve with a cellular structure characteristic of gas jets.

 While the findings outlined above support the theory presented in previous
works [42, 43, 44, 47], the consequence of these observations and implications
55 with respect to other propulsion and power systems is not clear. Thus, the ob-
jective of this paper is to now apply the theory to gain a clearer understanding
regarding the regimes present in other practical systems. This is accomplished
by performing a generalized analysis over a wider range of propellant combina-
tions (e.g., liquid-fuel–air in gas turbines and reciprocating engines, and liquid
60 oxygen–hydrogen for cryogenic rocket applications). A series of representative

interface profiles are calculated over a wide range of flow and mixture conditions. Substantial differences are demonstrated in species specific molecular properties, which result in distinct variations of two-phase interfacial structures and local mean free pathways. The systematic analysis leads to the derivation
65 of a more general regime diagram for liquid jet breakup that demonstrates when classical drop atomization and breakup regimes are being replaced by diffusion-dominated interfacial mixing for a range of conditions relevant in modern power and propulsion systems.

2. Model formulation

70 Details related to implementation of the theory to derive the regime diagrams of interest here is explained in detail by Dahms and Oefelein [43]. Thus, only a brief description is given here for brevity. The starting point of the model is based on the framework developed by Oefelein [48], which provides a generalized treatment of the thermodynamics and transport processes for hydrocarbon
75 mixtures at near-critical and supercritical conditions. This scheme is combined with the theoretical framework developed by Dahms *et al.* [42] and Dahms and Oefelein [43], which facilitates vapor-liquid equilibrium and gas-liquid interface structure calculations to compute both surface tension forces and the local two-phase interface thicknesses. Deriving the regime diagrams then involves the
80 implementation of thermodynamics and transport properties coupled with linear gradient theory to model respective interfacial structures. Following is a description of both of these frameworks.

A. Thermodynamic and Transport Properties

The development of equations of state has evolved in recent decades from
85 simple cubic and virial equations to Beattie-Bridgeman and Benedict-Webb-Rubin equations, and then to modified Benedict-Webb-Rubin and Helmholtz energy equations of state [49]. In this study, the extended corresponding states model [50, 51] is employed using a modified Benedict-Webb-Rubin (*BWR*) equa-

tion of state to evaluate the p - v - T behavior of the inherent dense multicomponent mixtures. Use of modified *BWR* equations of state in conjunction with the extended corresponding states principle has been shown to provide consistently accurate results over the widest range of pressures, temperatures and mixture states, especially at saturated conditions. Having established an analytical representation for real mixture p - v - T behavior, thermodynamic properties are obtained in two steps. First, respective component properties are combined at a fixed temperature using the extended corresponding states methodology to obtain the mixture state at a given reference pressure. A pressure correction is then applied using departure functions of the form given by Reid *et al.* [52, Chapter 5]. These functions are exact relations derived using Maxwell's relations (see for example VanWylen and Sonntag [53, Chapter 10]) and make full use of the real mixture p - v - T path dependencies dictated by the equation of state. Standard state properties are obtained using the databases developed by Gordon and McBride [54] and Kee *et al.* [55]. Chemical potentials and fugacity coefficients are obtained in a similar manner. Likewise, viscosity and thermal conductivity are obtained using the extended corresponding states methodologies developed by Ely and Hanley [56, 57]. Mass and thermal diffusion coefficients are obtained using the methodologies outlined by Bird *et al.* [58] and Hirschfelder *et al.* [59] in conjunction with the corresponding states methodology of Takahashi [60].

B. Vapor Liquid Equilibrium Theory

The real-fluid model for multicomponent mixtures is applied to obtain vapor-liquid equilibrium conditions. Assuming that the liquid is in thermodynamic equilibrium with its vapor, the equilibrium conditions are prescribed by the equality of temperature, pressure, and species chemical potentials between the vapor and liquid phases. Then, the critical point of a multicomponent mixture can be obtained as the point where the mixture compositions of the vapor and liquid phase become equal at supercritical pressures.

C. Linear Gradient Theory for Gas-Liquid Interface Structures

Gradient Theory provides a widely accepted methodology to calculate detailed interface structures between gases and liquids [61, 62]. At equilibrium, as applied in this paper, the model has been shown to be equivalent to mean-field molecular theories of capillarity. The foundation of this theory was established by van der Waals in 1893 [63, 64] and reformulated later by Cahn and Hilliard in 1958 [65]. Over past decades, Gradient Theory has been successfully applied to a wide variety of fluids: hydrocarbons and their mixtures, polar compounds and their mixtures, polymer and polymer melts, vapor-liquid and liquid-liquid interfaces. Recently, Gradient Theory has also been successfully compared to Monte Carlo molecular simulations of vapor-liquid and liquid-liquid interfaces [66, 67, 68]. There, Gradient Theory proved successful in capturing both surface tension and details of subcritical vapor-liquid molecular interfacial structures. It is worth pointing out that, for the simulation of molecular vapor-liquid interfaces, fundamental thermodynamic quantities such as pressure and chemical potential remain meaningful in Gradient Theory. Linear Gradient Theory has been derived from Gradient Theory by assuming a linearized minimization function of the Helmholtz free energy density distribution across the vapor-liquid interface for the calculation of the interfacial density profiles. Linear Gradient Theory has proven successful in calculating binary and multi-component interface states of the kind considered here [69, 70].

The interfacial profile of a planar multicomponent gas-liquid interface is obtained by minimizing the Helmholtz free energy, which is expanded as a Taylor series and truncated at lower spatial derivatives [62, 61]. The influence parameter, which determines the response of the density gradient to local variations of the species chemical potentials from their bulk value, is assumed to be density-independent [71] and is calculated based on the prior works of Lin *et al.* [61]. For temperatures higher than the critical temperature of the vapor component, the corresponding reduced temperature is set to a single value, consistent with suggestions from Zuo and Stenby [70]. This method has found wide acceptance and has also been adopted here [69] even though more suitable and generalized

methods have also been most recently proposed [72]. Using Gradient Theory,
 150 the surface tension and spatial interface dimension can then be calculated once
 the species density profiles within the interface have been obtained. In the limit
 of thermodynamic equilibrium, these profiles can be calculated by minimizing
 the Helmholtz free energy. The reference component over which the integration
 across the interface is performed is chosen as the liquid phase species. The
 155 boundary conditions of the bulk vapor and liquid phases for the interface cal-
 culation are obtained from real-fluid multicomponent vapor-liquid equilibrium
 calculations. Such equilibrium phase states account for solubility effects at high
 supercritical pressures. Then, the characteristic interface thickness is calculated
 following the criterion derived by Lekner and Henderson [73].

160 **3. Discussion**

The theoretical framework described above is used to perform a detailed
 analysis of the fundamental physics of two-phase interface dynamics for a vari-
 ety of mixture and flow conditions. The goal is to understand effects of species-
 specific molecular properties and to provide quantitative insights into liquid
 165 jet breakup regime transitions between classical spray atomization and dense-
 fluid diffusion-dominated mixing at elevated pressures. Using this theory, we
 consider the existence of two distinct physical conditions of interest. The first
 is the “classically assumed” situation when the gas-liquid interfacial structure
 (e.g., thickness) is much smaller than the molecular mean free path and thus
 170 the interface represents a jump discontinuity across which the governing Navier-
 Stokes equations are not valid. Corresponding states theory does also not apply
 for this condition, and instead we use phase equilibrium theory. The second
 condition is when the interface thickens to scales much greater than the molec-
 ular mean free path (as suggested by a Knudsen number criterion). At this
 175 condition, the interface itself becomes part of the continuum. Thus, both the
 Chapman-Enskog expansion procedure to the governing equations and the ex-
 tended corresponding states theory for related calculations of mixture properties

can be applied. It is important to recognize that phase equilibrium calculations do not provide insights into the spatial structure of the vapor-liquid interface. Here we have used Gradient Theory to provide these insights. Only in the case when the Knudsen number is approximately less than 0.1 (10 times thicker or more than the molecular mean free path) do we use corresponding states and the pseudo-critical values that are consistent with this theory (which are simply where the first and second partial derivatives of pressure with respect to specific volume are simultaneously zero), which is consistent with the notion that the entire mixture state is a continuum.

A select set of fuel-oxidizer combinations have been defined to bridge the fundamental analysis presented here to relevant conditions in modern propulsion and power systems such as liquid rockets, gas turbines, and reciprocating engines. The selected systems are summarized in Table 1. We analyze liquid-oxygen and gaseous-hydrogen, liquid n-decane and gaseous nitrogen, and liquid iso-octane and gaseous nitrogen, respectively. Liquid oxygen and gaseous hydrogen represent the actual fuel-oxidizer combination of many liquid rocket systems. The two hydrocarbons (n-decane and iso-octane) represent logical single component alkanes to model real-world fuels as they have properties meaningful for aviation fuel and gasoline. The carbon numbers of the selected fuels represent a characteristic mean for the widely acknowledged distribution in carbon numbers in real fuels, as shown in a recent work by Edwards [74]. This study also establishes a similarity in boiling range and density. For example, the density of JP-8 at 15 degrees Celsius is documented as approximately 0.795 kg/L, which is comparable to the density of decane at 15 degrees Celsius of 0.7344 kg/L. The mean of the boiling range of JP-8 is documented as $T = 420$ K, which also compares to the boiling point of decane at $T = 447$ K. Critical temperatures and critical pressures are also provided in this study. They deviate more substantially from the selected pure-fluid fuel properties. Real-world fuels are complex mixtures of hydrocarbons and alcohols and their full complexity has not been considered in this study. However, a meaningful similarity exists between the selected alkane and the real-world fuels.

	Liquid Rocket (H ₂)	Gas Turbine (C ₁₀)	Gasoline Engine (C ₈)
Binary Mixture	LO ₂ -GH ₂	LC ₁₀ -GN ₂	LC ₈ -GN ₂
Pressure (bar)	1 – 110	1 – 70	1 – 60
T _{Gas} (K)	100 – 400	350 – 1100	350 – 900
T _{Liquid} (K)	100	400	363

Table 1: Definition of the representative system of binary mixtures and flow conditions used to emulate realistic processes in advanced power and propulsion systems.

Figure 1: Saturation lines and critical points for all considered species.

Using the selected combination of liquid propellants summarized in Table. 1, interfacial properties are investigated for each fuel-oxidizer combination. To facilitate meaningful comparisons, the injection temperatures were chosen such that the reduced temperature of the injected liquid phase $T_L/T_{C,L} \approx 0.65$ remains constant. Based on this analysis, variations in species-specific liquid jet breakup regimes are quantified. To contrast differences in molecular properties, Fig. 1 presents the saturation curves for all of the pure species investigated in this analysis in a pressure-temperature diagram. The terms C_8 and C_{10} are abbreviations for the iso-octane and n-decane systems defined in Table 1. The term C_{12} is also included to represent n-dodecane for completeness since it was used as a single component alkane to represent diesel engine fuel in our initial study [43, 42]. The species-specific saturation lines end at the respective critical points. Several important trends in the critical properties of the liquid phase species are highlighted. The critical pressure decreases successively from oxygen to heavier hydrocarbons. The critical temperature shows the opposite trend. Additionally, the critical temperature of oxygen is higher than the critical temperature of hydrogen. Therefore, opposite to hydrocarbon-air systems, the oxidizer is injected as a liquid for the representative liquid rocket conditions considered here.

To compare the different fuel-oxidizer combinations in a meaningful way, the mixture fraction is consistently defined as the mass fraction of the corresponding fuel in the local mixture. Using the equation of state and corresponding mixing rules, thermodynamic mixture properties such as the compressibility factor, enthalpy, and fugacity coefficient are obtained. Then, vapor-liquid equilibrium conditions can be calculated. Figure 2 (top) shows envelopes of temperature-mixture compositions for a binary oxygen-hydrogen system at different pressures (as one representative example). These curves illustrate that the critical temperature decreases with increasing pressure beyond the critical pressure of the liquid phase. Similarly, Fig. 2 (bottom) further highlights the maximal temperatures under which a two-phase system can be maintained as a function of pressure for all investigated mixtures. At pressures subcritical with respect to

Figure 2: (Top) Vapor-liquid equilibrium conditions for an oxygen-hydrogen system at different pressures as a function of temperature and fuel (H_2) mixture fraction. (Bottom) Liquid boiling T_{Boil} and vapor-liquid critical temperatures T_c for the defined fuel-oxidizer combinations as a function of pressure.

Figure 3: Fuel mole fraction at liquid phase boiling temperatures and critical mixing temperatures for subcritical and supercritical liquid phase pressures, respectively. Note that the liquid phase boiling temperature is the maximal temperature under which a two-phase system can be maintained at subcritical liquid phase pressures, compare Fig. 2 (bottom).

the liquid, this temperature corresponds to the boiling temperature of the liquid phase (as shown in Fig. 1). At pressures supercritical with respect to the liquid, however, it represents the critical mixing temperature of the binary system. This critical mixing temperature decreases linearly with pressure as the gas dissolves into the liquid phase.

Figure 3 shows that the mole fractions of the fuel at the critical condition consistently decrease (for the hydrocarbons) and increase (for gaseous hydrogen fuel) asymptotically with pressure for all mixtures. The combination of the equation of state with vapor-liquid equilibrium calculations provide the compositions and mixture states of the respective vapor and liquid phases at given temperature and pressure conditions. To obtain information about the spatial distribution of the species compositions across the interface Linear Gradient Theory is applied. Calculations of vapor-liquid equilibrium specify the homogeneous phase vapor and liquid properties, which serve as boundary conditions in the computations. The accuracy of the method for systems considered here is demonstrated in [43, 69].

Figure 4 presents the molecular mean-field density profiles within gas-liquid

Figure 4: Molecular mean-field density profiles within two-phase interfaces for different mixtures, defined in Table 1, at constant pressure and two different reduced temperatures.

Figure 5: Mean-field molar density profiles and molecular mixture fraction distribution across the two-phase interface of a C₈–N₂ mixture at pressure p=60 bar and reduced temperatures T_r=0.85.

interfaces for different mixtures at constant pressure, supercritical with respect to all liquids, and at two different reduced temperatures. The mixtures are defined in Table 1. Consistent with vapor-liquid equilibrium and Gradient Theory
260 assumptions, the temperature is assumed to be constant across the molecular interface. Trends in the figure show that the molecular density profiles of all mixtures have a similar hyperbolic tangent shape. The liquid density of oxygen is higher than corresponding densities of the hydrocarbon fuels. Likewise, the density ratio of the oxygen-hydrogen mixture is higher in comparison to
265 the other systems. It is also shown that an increase in alkane carbon number results, under constant reduced temperature conditions, in a slight increase in liquid density and in the formation of thinner interfaces. With increasing temperature, as shown in Fig. 4 (bottom), the liquid densities decrease and the two-phase interface broadens substantially.

270 As an illustrative example, Fig. 5 shows the molecular mean-field fuel mixture fraction distribution and molar density distribution of a C₈–N₂ mixture, defined in Table 1. The molecular mixture fraction $\hat{Z}$ is defined as

$$\hat{Z} = \frac{\rho_{C_8}}{\rho_{C_8} + \rho_{N_2}} \quad (1)$$

Figure 6: Representative interface thicknesses, computed using the theoretically determined criterion from Lekner and Henderson [73] for all mixtures at constant pressure as a function of the reduced temperature.

with ρ as the mean-field species mass density calculated by Gradient Theory.

The effect of temperature on the interface thickness is investigated in more
 275 detail in Fig. 6. Representative interface thicknesses, calculated using the theoretically determined criterion from Lekner and Henderson [73], are shown at constant pressure as a function of the reduced temperature. At these supercritical pressures, the critical temperature was previously shown to be a function of the pressure (see Fig. 2 (bottom)). A similar exponential growth of the thick-
 280 ness of gas-liquid interfaces with increasing reduced temperature is consistently observed for all investigated mixtures. However, some differences exist. The required reduced temperature for a certain interface thickness increases with carbon number for alkane fuels. In combination with the likewise increase in critical temperature, compare Fig. 1, this analysis shows that higher alkane car-
 285 bon number fuels are required to be heated to substantially higher subcritical temperatures in order to broaden their two-phase interfaces in equal measure.

After investigating differences in two-phase dynamics that result from variations in vapor-liquid equilibrium conditions and interfacial molecular density

Figure 7: Adiabatic mixing temperatures of the fuel-oxidizer combinations, defined in Table 1, at constant pressure. The temperatures of the respective streams are chosen as meaningful values in corresponding power and propulsion system.

profiles due to different fuel-oxidizer combinations, single-phase mixing processes are analyzed in the following. First, a unique relationship between fuel mixture fraction and temperature is established by assuming adiabatic mixing [42, 43]. Then, the enthalpy becomes a linear function of mixture fraction. The mixture state equation is applied to obtain the adiabatic mixing temperature for each mixture fraction by matching the resulting mixture enthalpy to the prescribed enthalpy distribution. Figure 7 illustrates resulting adiabatic mixing lines for the investigated fuel-oxidizer combinations at constant pressure. Temperatures of the respective fuel and oxidizer streams have been chosen as representative values in the corresponding power and propulsion system of interest. Substantial differences in the temperature distribution exist between liquid rockets, where the oxidizer is typically injected as a liquid at about 100 K, and gas turbines or gasoline and diesel engines, where the fuel is injected as a liquid typically at about 400 K and 363 K, respectively, into a high-temperature gaseous environment. Some less significant differences among the mixing lines of the hydrocarbon-nitrogen systems are also highlighted in the inset-plot of Fig. 7.

Figure 8: Illustration of a representative vapor-liquid equilibrium condition in a liquid rocket engine. This condition is restrained by the chamber pressure, which defines the envelope of possible vapor-liquid equilibrium conditions, and the adiabatic mixing line, which defines the envelope of possible vapor states.

To bridge the gap between single-phase and two-phase processes, the adiabatic mixing lines are superimposed onto the corresponding vapor-liquid equilibrium lines. The reasoning is that adiabatic mixing lines represent the envelope of conditions under which a vapor state of a two-phase vapor-liquid equilibrium condition can exist. The vapor mixes with the ambient gas and this process has to obey to the available enthalpy distribution in the system. Likewise, the chamber pressure restrains the envelope of conditions under which a vapor-liquid equilibrium is possible. Figure 8 illustrates a representative vapor-liquid equilibrium condition in a liquid rocket engine. The chamber pressure and the resulting interface temperature, here $T \approx 126$ K, defines the precise two-phase interface condition which is used as a boundary condition for Linear Gradient Theory to reconstruct the molecular interface structure. Then, the thickness of the interface is computed. Additionally, the mean free pathway in the vapor state has to be quantified.

Previously, it was shown that under some conditions the vapor mean free path can become substantially shorter than the interface thickness so that the

Figure 9: Reduced two-phase interface temperature as a function of pressure for the investigated fuel-oxidizer systems. Note that the critical mixing temperature T_C is a function of pressure as demonstrated in Fig. 2 (bottom).

two-phase interface may enter the continuum regime. Under the presence of substantial temperature gradients, the vapor does not equilibrate with the liquid anymore and the vapor-liquid equilibrium assumption becomes questionable.

325 This condition was quantified using an interface Knudsen-number criterion [42, 43]

$$\text{Kn} = \frac{\lambda_V}{\ell} < 0.1 \rightarrow \text{Continuum Regime [75]}. \quad (2)$$

Here λ_V is the mean free path in the vapor, defined in [42, 43], and ℓ is the characteristic interface thickness.

Figure 9 shows the reduced two-phase interface temperatures as a function
 330 of pressure for the investigated fuel-oxidizer systems. This reduced temperature is defined as the ratio of the actual temperature of the interface and its critical temperature. At pressures in excess of the critical pressure of the liquid, this critical temperature decreases linearly with pressure (compare Fig. 2, bottom). The analysis shows that higher chamber pressures generally lead to
 335 higher reduced interface temperatures for all mixtures. For equal chamber and injection conditions, this reduced temperature decreases with an increase of the

fuel carbon number. Furthermore, the increase of the reduced temperature with pressure also decreases with the fuel carbon number. The curve for the liquid-oxygen-gaseous hydrogen mixture starts at pressures beyond $p=p_{C,O_2} \approx 5.04$ MPa, since pressures subcritical with respect to the liquid phase are not considered here.

In the following, the analysis of interface dynamics is restricted to two-phase interfaces which enter the continuum regime, verified by the Knudsen-number criterion defined in Eq. (2). Then, both the mixture fraction and the temperature are well-defined and vary continuously across the interface which evolves into a dense-fluid mixing layer. The mixture state equation can then be applied to compute the mixing layer's adiabatic mixture state conditions across the whole mixture fraction space as exemplified in Fig. 10. Assuming that the liquid (L) is in thermodynamic equilibrium with its vapor (V), the equilibrium conditions are prescribed by $T^V = T^L$, $p^V = p^L$, and $\mu_i^V = \mu_i^L$. The envelope of such vapor-liquid equilibrium conditions for a n-dodecane–nitrogen system at $p=60$ bar was analyzed in detail by Dahms *et al.* [43, 42, 44]. Results for this case are shown in Fig. 10. The interface temperature is obtained as the intersection point between the adiabatic mixing temperature and the vapor equilibrium temperature. Note that vapor-liquid equilibrium theory dictates a constant temperature across the molecular interface as highlighted in Fig. 10. Under the conditions here, however, this interfacial region enters the continuum length scale regime where it departs from such equilibrium conditions. As a consequence, adiabatic mixing temperatures are used to represent the relationship between temperature and fuel mixture fraction as illustrated in Fig. 10.

Informed by this analysis, the equation of state can then also be used to compute the critical line of the mixture as the envelope of conditions where the temperature T and pressure p are equal to the critical temperature of the mixture $T_C(Z)$ and critical pressure of the mixture $p_C(Z)$ of the corresponding mixture state. Along this critical mixing line, the pseudo-pure fluid assumption ($x'=x''$; x' : Liquid mole fraction; x'' : Vapor mole fraction) of the mixture state equation is fulfilled. Pseudo-pure fluid saturation lines for each mixture state

Figure 10: Adiabatic mixing line, vapor-liquid equilibrium conditions, and isothermal molecular interface line between vapor and liquid for a n-dodecane–nitrogen system at $p=60$ bar. N-dodecane is injected as a liquid at $T_F=363$ K into gaseous nitrogen at $T_A=900$ K.

are computed in a manner consistent with the extended corresponding states model.

Figure 11 shows the envelope of such saturation points for oxygen-hydrogen mixtures. The thermodynamic regimes can be defined using a pure fluid analogy. Subcritical temperatures and pressures define liquid and vapor states. Supercritical temperatures and pressures define the supercritical state. Supercritical temperatures and subcritical temperatures define an ideal gas. Supercritical pressures and subcritical temperatures define the compressed liquid phase. Pressures and temperatures are defined supercritical or subcritical for each mixture state if they are higher or lower than corresponding values of the critical line of the mixture defined in Fig. 11. This line forms the locus of critical temperatures and pressures of each mixture state in a manner consistent with corresponding states theory. They have been calculated directly from the equation of state as the points where the first and second partial derivative of the pressure with respect to the density, evaluated at constant temperature, are both zero for all

Figure 11: Pseudo-pure fluid mixture saturation surface, calculated consistent with the assumptions of the extended corresponding states theory, for oxygen-hydrogen mixtures that defines the critical line of the mixture.

mixture states; i.e.,

$$\left(\frac{\partial p}{\partial \rho}\right)\bigg|_{T|_{T_C, \rho_C}} = \left(\frac{\partial^2 p}{\partial \rho^2}\right)\bigg|_{T|_{T_C, \rho_C}} = 0 \quad (3)$$

It is again stressed that Eq. (3) has a physical meaning only for a multi-
 385 component mixture in a continuum as quantified by Eq. (2). In a classical
 two-phase system, this state is not realizable and vapor-liquid equilibrium the-
 ory provides the appropriate method to calculate critical properties; see for
 example Delplanque and Sirignano [76] or Peng and Robinson [77]. The critical
 values of the mixture according to Eq. (3) are presented in Fig. 12. The critical
 390 properties approach the corresponding pure fluid values at fuel mixture frac-
 tions $Z=0$ and $Z=1$, respectively. For the investigated hydrocarbon systems,
 the critical temperature of the mixture increases with mixture fraction. For
 mixture fractions lower than $Z \approx 0.5$, the differences among the hydrocarbon
 fuels diminish. Such differences prevail, however, in the critical pressure across
 395 the whole mixture fraction space. Here, an increase in alkane carbon number
 fuels result in a decrease in the corresponding critical pressure of the mixture.
 For the oxygen-hydrogen system, the distributions of the critical values of the
 mixture are reversed. Both critical temperature and critical pressure of the
 mixture decrease with fuel mixture fraction. The conceptual picture here is
 400 in contrast to the calculation of the critical point based on vapor-liquid equi-
 librium, as illustrated for example in Fig. 10. Here, the critical point for the
 same mixture composition is calculated directly from the equation of state in a
 manner consistent with the assumptions of the extended corresponding states
 theory. This method is based on homogeneous-fluid assumptions and, as such,
 405 explicitly assumes that the two streams mix and do not form a distinct molecular
 interface.

Figure 13 presents the calculated reduced supercritical mixture pressure as
 a function of the reduced gas temperature for a specific reduced liquid injection
 temperature for the investigated fuel-oxidizer combinations. The reduced gas
 410 temperature is defined as the temperature of the gas that the liquid is injected
 into normalized by the critical temperature of the liquid phase. This figure illus-

Figure 12: Critical temperature of the mixture (top) and critical pressure of the mixture (bottom) for the investigated fuel-oxidizer combinations, defined in Table 1. It is stressed that these critical values, calculated from Eq. (3), have a physical meaning only for a multi-component mixture in a continuum as quantified by Eq. (2). In a classical two-phase system, vapor-liquid equilibrium theory provides the appropriate method to calculate critical properties [76, 77].

Figure 13: Reduced supercritical mixture pressure as a function of the reduced gas temperature for a certain reduced liquid injection temperature for the investigated fuel-oxidizer combinations. The supercritical mixture pressure of the oxygen-hydrogen system is constant and equal to the critical pressure of pure oxygen. Note that the application of Eq. (3) is only meaningful when the interface has entered the continuum regime at $Kn < 0.1$, compare Eq. (2).

Figure 14: Spray/dense-fluid regime transitions of liquid oxygen injection at a temperature $T=100$ K along with a gaseous hydrogen coaxial injection. The range of pressures and temperatures are representative of liquid rocket operating conditions.

trates that the reduced supercritical mixture pressure increases with the alkane fuel carbon number and decreases with the reduced gas temperature. Considering the species-specific critical pressure, however, the actual pressure to support a continuous phase transition from compressed liquid to supercritical mixture states decreases with fuel carbon number. Even though the ratio $p_{c,mix}/p_{L,c}$ increases from the octane system (C_8) to the dodecane (C_{12}) system, the required chamber pressure $p_{c,mix}$ decreases due to the much lower critical pressure $p_{L,c}$ of C_{12} in comparison to C_8 as highlighted in Fig.1. Interestingly, the analysis also shows that the supercritical mixture pressure of the oxygen-hydrogen system is constant and equal to the critical pressure of pure oxygen.

In the following, the conditions under which liquid jet breakup regimes of classical sprays transition to single-phase atomization of dense-fluid jets are quantified using pressure-temperature charts for each set of selected fuel-oxidizer combination. Corresponding transition conditions result from the envelope of interface Knudsen-number isolines $Kn=0.1$, as defined in (2), and the super-

critical mixture pressures, obtained from Fig. 13. Figure 14 shows such liquid jet breakup regime transitions for a range of pressures and temperatures which are representative of liquid rocket operating conditions. The considered configuration emulates a liquid oxygen injection at a temperature of $T_{O_2}=100$ K along with a shear-coaxial injection of gaseous hydrogen into a combustion chamber [3, 4, 78]. Then, the hydrogen temperature is independent from the chamber pressure, demonstrated by the two constant hydrogen temperature injection conditions of $T_{H_2,1}=150$ K and $T_{H_2,2}=300$ K shown in Fig. 14. Isolines of different Knudsen-numbers are presented that span a reasonable range of uncertain interface behavior [43]. The regime diagram shows, consistent with observations reported by Mayer *et al.* [3], that classical sprays transition to dense-fluid jets at chamber pressures comparable to the critical pressure of oxygen ($p_{C,O_2} \approx 5.04$ MPa) when hydrogen is coaxially injected at $T_{H_2}=300$ K. It is important to realize that this conclusion has been obtained by considering the multicomponent multiphase interface dynamics. By coincidence, the analysis obtains results which are, under the conditions here, similar to those of a pure fluid analogy model for multicomponent mixtures. In pure fluids, surface tension forces diminish, independent of the temperature, when the pressure exceeds its thermodynamic critical pressure. However, as demonstrated in this paper and elsewhere [43, 42], such a pure fluid analogy is generally invalid for multicomponent mixtures.

Figure 15 presents conditions of spray/dense-fluid regime transitions of liquid injection for a range of pressures and temperatures representative of gas turbines. Liquid n-decane, an approximate single component alkane for jet-A fuel, is injected at a temperature $T_L=400$ K into a pressurized nitrogen chamber. The turbine compressor increases the pressure of the ambient air before it enters the combustion chamber. Within the compressor stage, the gas undergoes a polytropic compression, which also results in an increase in gas temperature. Then, the gas temperature becomes, in contrast to the liquid rocket configuration, dependent on pressure. Thus, Fig. 15 highlights relevant gas turbine compressor outlet conditions that represent characteristic pressure-temperature

Figure 15: Spray/dense-fluid regime transitions of liquid n-decane (C_{10}) injection at a temperature $T=400$ K into a gaseous nitrogen environment. The range of pressures and temperatures are representative of gas turbine operating conditions.

conditions of the air entering the combustion chamber [79]. The diagram also shows isolines of meaningful interface Knudsen-number values along with the corresponding supercritical mixture pressure. Interestingly, the regime diagram suggests that, contrary to conventional wisdom, diffusion dominated mixing, instead of classical atomization and spray processes, occur at relevant high-pressure ($p > 35$ bar) gas turbine conditions.

Figure 16 presents conditions of spray/dense-fluid regime transitions for a range of pressures and temperatures representative of gasoline direct-injection spark-ignition engine operation. The detailed specifications of those engine operating conditions under development by engine manufacturers can be found elsewhere [14, 9, 23]. In such modern gasoline engines, the fuel is injected directly into a cylinder that is usually charged with a combination of fresh air and recirculated exhaust gas. The time of fuel injection determines the pressure-temperature conditions of the ambient gas as it is being compressed due to the piston motion. This process is represented in the diagram as a polytropic com-

Figure 16: Spray/dense-fluid regime transitions of liquid iso-octane (C_8) injection at a temperature $T=363$ K into a gaseous nitrogen environment. The highlighted range of pressures and temperatures are representative for current gasoline direct-injection spark-ignition engine operation.

pression. Furthermore, typical cylinder gas conditions for varying spark-ignition engine operation are highlighted [23, 24, 36, 18, 80]. Isolines of meaningful interface Knudsen-number values along with the supercritical mixture pressure mark the conditions where classical sprays transition to dense-fluid jets. The diagram shows that classical spray phenomena are expected to prevail under current gasoline direct-injection engine operation. Direct injection of gasoline into the combustion chamber takes place at chamber pressures substantially lower than the supercritical mixture pressure.

After investigating the spray/dense-jet transition conditions for advanced propulsion and power systems using device-specific operating conditions, Fig. 17 compares the differences associated with the various fuel-oxidizer combinations in a general manner. A diagram is derived for a specific reduced liquid injection temperature as a function of reduced gas temperature and pressure. The gas temperature is normalized by the liquid phase critical temperature. As established in Fig. 6, the two-phase interface thickness scales mainly with the reduced

Figure 17: Spray/dense-fluid regime transition lines result from interface Knudsen-number iso-lines $Kn=0.1$, defined in (2), and from supercritical mixture pressures, obtained from Fig. 13. The fuel-oxidizer combinations are compared for a certain reduced liquid injection temperature as a function of reduced gas temperature and pressure.

interface temperature which depends on, at constant liquid injection conditions, the gas temperature and the liquid phase critical temperature. Both of these quantities then establish the abscissa of the liquid injection regime diagram. The diagram illustrates that the envelope of spray/dense-fluid transition conditions exhibit a similar characteristic shape for all fuel-oxidizer combinations. The precise location of the Knudsen-number isolines depends on the mixture composition and chamber pressure and shows a substantial sensitivity to the chamber temperature. At pressures just above the supercritical mixture pressure, the analysis establishes that the chamber temperature is required to exceed the critical temperature of the injected liquid phase.

Informed by this analysis, the regime diagram for liquid jet breakup at elevated pressures is introduced in Fig. 18. It is based on the same definition for the abscissa and ordinate as applied in Fig. 17. The representative spray/dense-fluid regime transition line $\overline{\text{Kn}}=0.1$ is established as the average of the Knudsen-number lines shown in Fig. 17. Such an averaged location is representative and meaningful due to the similar characteristic shapes with only moderate variations of the individual species-specific isolines, demonstrated for a wide range of fuel-oxidizer combinations in Fig. 17. Then, the envelopes of typical high-pressure operating conditions in gasoline direct injection engines, gas turbines, and diesel engines are highlighted in the regime diagram. The analysis demonstrates that single-phase dense-fluid injection dynamics, instead of the widely assumed classical spray and atomization processes, may occur under many relevant high-pressure conditions in modern gas turbines and diesel engines. Classical spray atomization processes prevail in current gasoline direct injection engines. It is worth noting, however, that current trends in gasoline engine development such as downsizing and turbo-charging will likely further increase the in-cylinder pressure which may make corresponding direct injection processes also subject to dense-fluid injection dynamics.

It is essential to realize that hot unburnt gas temperatures do not, as previously demonstrated [40, 41, 42, 43], actually heat the interface to its critical value. However, supercritical temperature gas conditions lead to high subcrit-

Figure 18: Regime diagram for liquid jet breakup at elevated pressures. The representative spray/dense-fluid regime transition line is obtained as an average interface $\overline{Kn}=0.1$ isoline, making use of the similar characteristic envelopes of species-specific isolines as demonstrated in Fig. 17. The range of typical high-pressure operating conditions in modern power and propulsion systems is highlighted.

ical gas-liquid interface temperatures (compare Figs. 10, 8, and 9). These are
520 required to substantially broaden the two-phase interface (compare Fig. 6). This
broadening is essential in the initiation of the transition from classical sprays
to dense-fluid jets as it determines the interface Knudsen-number. With in-
creasing pressure, however, the mean free pathway continues to shorten sub-
stantially. Then, even thinner two-phase interfaces at lower reduced subcritical
525 temperatures, caused by cooler ambient gas, can enter the continuum regime.
Hence, the required gas temperature can drop below the critical temperature
of the liquid phase. As illustrated in Fig. 17, this is particularly true for the
oxygen-hydrogen system. For alkane fuels, the analysis shows that the required
pressure-temperature conditions for a breakdown of the two-phase interface in-
530 creases with carbon number despite the simultaneous decrease in critical pres-
sure (compare Fig. 1). Higher hydrocarbon fuels have an increasingly high den-
sity and form thinner interfaces, as shown in Fig. 4 and 6. Hence, the required
reduced interface temperature increases with the carbon number in order to
compensate for this physical complexity. The simultaneous reduction in liquid
535 phase critical pressure with carbon number which increases the reduced inter-
face temperature (compare Fig. 2 (bottom) and 9) cannot compensate for this
effect. Hence, the absolute ambient gas temperature, the liquid is injected into,
has to increase to maintain constant interface Knudsen numbers. This analysis
then also explains why supercritical ambient gas pressure and temperature con-
540 ditions with respect to the liquid phase critical properties are usually required
to initiate the transition to dense-fluid mixing, even though the vapor-liquid
interface does not actually reach supercritical conditions.

4. Conclusions

In this paper, a comprehensive analysis of liquid jet breakup regimes at ele-
545 vated pressures and for different mixture and flow conditions has been presented.
The analysis uses a generalized framework for multicomponent mixtures based
on theories of capillary flows and extended corresponding states. It was shown

that the multiphase interfacial structures vary substantially for different mixture and flow conditions. However, a similar exponential growth of the thickness
550 of these interfacial structures with respect to the reduced interface temperature was consistently observed. This growth was shown to scale inversely with the pressure-dependent critical temperature of the dissolved liquid phase. In combination with substantial differences in species-specific molecule size, chemical potential, and critical properties, the analysis establishes that the proposed fundamental theory on liquid jet breakup regimes of multicomponent fluids is valid
555 for a wide range of different fuel-oxidizer combinations.

At pressures lower than the mixture saturation limit, which quantifies the mixture-specific operating pressure to support a continuous phase transition from compressed liquid to supercritical mixture states, classical spray phenomena generally prevail. A well-defined molecular two-phase interface exists and promotes the widely acknowledged atomization, spray, and drop evaporation processes due to the presence of surface tension forces. At higher pressures, however, the two-phase interface can enter the continuum length scale regime where surface tension forces become diminished as the interfacial region substantially grows in thickness while the mean free molecular path decreases due
565 to pressure. This consistently occurs for all investigated mixtures. Then, nearly-linear gradients over molecular distances develop within the interfacial region. Consequently, the set of vapor-liquid equilibrium assumptions along with the embedded notion of a distinct two-phase interface become questionable.

570 The conditions where regimes of classical drop deformation and breakup are replaced by single-phase atomization were quantified by deriving system specific regime diagrams for common liquid-gas systems. It was shown that the envelope of such transition conditions depends on molecular quantities and exhibits a characteristic shape for all selected binary mixtures. Different sets of fuel-oxidizer mixtures and operating conditions were analyzed to demonstrate
575 the significance of this theory for modern propulsion and power systems. The analysis suggests that single-phase dense-fluid injection dynamics, instead of the widely assumed classical spray and atomization processes, occur under many rel-

evant device conditions. Then, the concept of classical spray and drop models
580 becomes questionable. Instead, non-ideal real-fluid thermodynamics and transport must be taken into account that apply at such high-pressure single-phase conditions.

The analysis presented here applies to binary mixtures and builds on single component alkanes as fuel surrogates. Real-world fuels, however, are complex
585 mixtures of hydrocarbons and alcohols and their full complexity has not been considered in this study. The modeling of such realistic fuel mixtures presents a challenging task in part due to the complex phase behavior of the non-ideal mixtures and the requirement to obtain their direct-correlation functions, which are significantly affected by cross-collision forces. This analysis also assumes homo-
590 geneous pressure and temperature distributions in the liquid phase and ambient gas, which does not fully represent the complex conditions in actual devices. However, much of this physical complexity can be recovered if different mixture regions are associated with different locations within the regime diagram.

5. Acknowledgement

595 This research was funded by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, US Department of Energy. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94-AL85000. This research was performed
600 at the Combustion Research Facility, Sandia National Laboratories, Livermore, California.

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