Mixing and Combustion in Dense Mixtures

by William A. Sirignano and Derek Dunn-Rankin

At very high pressures and densities, what is different and what is similar about the processes of – Injection and Atomization, Phase Change, Molecular Transport, Turbulent mixing, Oxidation, and Soot Formation – and the Abilities for Modelling and Measurement.
What do we mean by “high pressure”?

- *High density is actually meant.*
- In particular, density is so high and molecular distances so small that molecular force fields reach beyond the distance to neighboring molecules.
- Since molecular collisions become continuous rather than intermittent, the ideal gas law must be abandoned. A cubic equation of state is commonly used, e.g., van der Waals, Peng-Robinson, or Redlich-Kwong.
- Certain mixing rules are needed in the state equation applied to multicomponent fluids to determine two “constants” which actually vary over space and time with composition.
Two phases or a continuous fluid?

- *It is widely and often wrongly assumed that a liquid injected into a surrounding gas at a subcritical liquid temperature but supercritical pressure for all components, may always be treated as a continuous fluid.*

- The critical pressure of a mixture can be several times greater than the critical values for the components. Thus, critical pressure becomes a variable over the domain as composition varies and many problems must be viewed as transcritical with both subcritical and supercritical subdomains.

- Near the critical point, gas more easily dissolves in liquid and liquid more easily vaporizes; surface tension and energy of vaporization are reduced. Both phases must be considered as mixtures.

- *Whether we have a distinct liquid phase with a distinct gas phase or one continuous fluid without interfaces, transport of mass will be important because of composition gradients. Heat transport will occur because of inherent temperature gradients.*
Hydrocarbon – $O_2$ mixtures
Two-phase behavior at up to 7x “critical” pressures

Computed by Albert Jordà Juanós

Propane ← Heptane
Octane ← Decane
Mixture of decane, O₂, N₂, CO₂, and H₂O at 4x the critical pressure of decane. Two phases clearly exist!!

A. Jordà Juanós
Surface Tension for near-critical behavior
Value depends on all components

Surface tension depends strongly on liquid temperature, more modestly on pressure and ambient gas temperature.

Calculation by Delplanque & Lengsfeld -- Heptane-Nitrogen
Enthalpy of Vaporization

-- Latent heat of vaporization applies exactly to single species systems. Enthalpy of vaporization is needed for multispecies systems.

-- Enthalpy of vaporization decreases with increasing temperature and increasing pressure.

V. Yang & Co-workers  A. Jordà Juanós
Density versus composition in a two-component decane-O2 mixture at subcritical temperature and a pressure supercritical for each component.

A fuzzy zone in images may or may not have a discontinuous density.
Breakup of Injected Fuel Stream (aka atomization) at High Reynolds and Weber numbers

• The disintegration of the injected fuel stream determines the chamber mixture ratio distribution.

• The process also determines length scales for the resulting fuel droplets, ligaments, or ‘blobs’ thereby affecting rate controlling processes such as vaporization and mixing.

• *Thus, without knowledge of these processes, we have no starting point for practical combustion analysis.*

• Except for final stages, the atomization process is weakly dependent on surface tension and viscosity.

• Consequently, substantial similarities are found for homogeneous jets (e.g., air-into-air or water-into-water) and liquid jets into gas.
Round jets with 3D instabilities of axisymmetric vortex rings

Liepmann & Gharib (1992), water-into-water


Vorticity analysis shows common cause between the above side jets and the ligaments and lobes to the left.
**Liquid transient, round jet into still air**

*Shinjo & Umemura (2010), NS-LS*

\[ Re = 440 \text{ – } 1470; \ We = 1270 \text{ – } 14,100 \]

*Jarrahbashi & Sirignano (2014), NS-LS-PP*

\[ Re = 1600 ; \ We = 230000 ; \ \rho_1 \ / \ \rho_2 = 0.1 \]

-- Cap forms on starting jet.
-- Mass and size of cap increase.
-- Instability causes shredding of cap.

-- Cones have azimuthal instability. Lobes form.
-- Lobes stretch and tear under azimuthal instability.
-- Ligaments form from torn rims.
-- Capillary instabilities on ligaments.
Density ratio affects 3D instability but a qualitative similarity exists over a wide range. *There is no basis for assuming large qualitative distinction in cone, lobe, and ligament formations for supersonic injection at low Mach numbers.*

\[
\begin{align*}
Re & = 1600 \\
We & = 230,000 \\
\mu_1 / \mu_2 & = 9 \times 10^{-4} \\
t & = 90 \mu s
\end{align*}
\]

\[
\rho_1 / \rho_2 = \begin{cases} 
0.1, & 0.5, & 0.9 
\end{cases}
\]
Turbulent Mixing

- *Molecular transport remains important even with turbulent eddies enhancing mixing.*
- The temporal and spatial behavior within a two-dimensional viscous vortex placed at the interface between reactants is analyzed. Diffusion across the strained material lines is determined.
- *Mixing rates increase with both vortical strength (circulation) and diffusivities for heat and mass.*
- Results can be shown for the mixing of two nonreacting fluid species and for the mixing with reaction of two reactants and a product.
- A mixedness parameter $f(t)$ is used based on integrations over the volume eddy: $f(t) = \frac{\langle C_1 C_2 \rangle}{[\langle C_1 \rangle \langle C_2 \rangle]}$ where $C_1$ and $C_2$ are concentrations and $\langle \rangle$ implies an instantaneous volume average. With complete mixing $f = 1$; with no mixing, $f = 0$. 
Two-dimensional Eddy Mixing, Cetegen & Sirignano

\[ Sc = 1, \ (D = \nu) \quad ; \quad R = \Gamma / \nu \]

A PDF is formed by averaging over \( x \). \( P(C, y, t) \) is formed with mixing in core. Clearly, a dependence on mass diffusivity as well as vortex circulation results.
Mixedness Parameter

Mixedness enhancement $\Delta f$ due to eddy circulation and strain increases with time, vortex strength, and mass diffusivity.

$$D = \nu ; \quad R = \Gamma / \nu$$
Turbulent Mixing of O₃ and NO with isothermal chemical reaction

For reacting case, similar conclusions occur about dependence of mixedness on both vortex strength and molecular transport.
Molecular Transport

Water – dramatic effects near the critical point diminishing at more extreme conditions.
Prandtl Number of Binary Mixtures of Noble Gases

-- Complex behavior for mixtures, strongly nonlinear behavior.
-- Variable mixture ratios over space and time gives highly non-uniform transport properties.
-- Beware of simplifying assumptions.
-- Sub-grid models become huge challenge.

Tournier & El-Genk, 2008
Challenges with Molecular Transport

• Transport properties of mixtures are complex.
• More information about properties for mixtures of combustion reactants and products is needed.
• Discontinuities with phase change are replaced by regions of steep gradients at supercritical conditions.
• Viscosity can decrease with increasing density causing higher Reynolds numbers, smaller scales of turbulence, and greater demands on sub-grid modelling.
Vaporization

A cold fuel droplet might be sub-critical for its local gas mixture.---A discontinuity in composition and density exists at the interface.---For a hot environment, critical temperature occurs at some distance.---Eventually, after some heating and vaporization, the critical surface reaches the interface. Phase distinction ceases.
Challenges with Near-critical Vaporization

-- Enthalpy of vaporization and surface tension still exist, can be important, and more difficult to calculate because they are mixture-dependent.
-- Gases dissolve in liquid and diffuse through liquid, creating a multicomponent liquid-phase diffusion problem.
-- A quasi-steady gas-phase assumption becomes unreasonable; magnitudes of transport properties are similar in both phases which now must be considered unsteady.
-- The droplet heating and vaporization problem becomes much more difficult.
Chemical Reactions

- While oxidation rates increase with density, transport rates decrease possibly modifying rate control in some situations.
- At high densities, new pathways must be evaluated.
- Can chemical kinetic theory be built around bi-molecular and tri-molecular collisions for a dense gas with continual rather than intermittent collisions?
- Use fugacity, not partial pressure, in law of mass action for chemical equilibrium.
- How can kinetic laws without fugacity variables predict chemical equilibrium?
Summary of Key Knowledge

• It is high density, not high pressure!
• Molecular transport is always important in mixing and combustion problems, whether turbulent or laminar, continuous phase or two phase.
• Molecular transport is generally slower, more controlling at high density.
• Two-phases can exist at pressures well above the critical pressures of any component in a mixture.
• Substantial mixing occurs across phase interface; thus, fuzzy, blurry images need not imply a continuous phase.
• Length scales for composition variation and distribution of mixture ratio are vital characteristics for composition; thus, whether two-phase or continuous phase, “atomization” is important.
• For the first stages of atomization, vorticity dynamics is controlling while viscosity and surface tension are of little importance; thus, there is little difference amongst homogeneous jets (e.g., water-into-water), liquid jets into gas, and continuous-phase high-density jets.
• Vaporization is a more complex problem at high densities and still is potentially rate-controlling.
Knowledge Gaps for High-density Flows

• Atomization in the near-critical two-phase domain.
• “Atomization” in the continuous fluid domain.
• Sub-grid (small length-scale) mixing models.
• Trans-critical vaporization models.
• Chemical pathways.
• Thermophysical and transport properties for MIXTURES at high density.
Thank You