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.

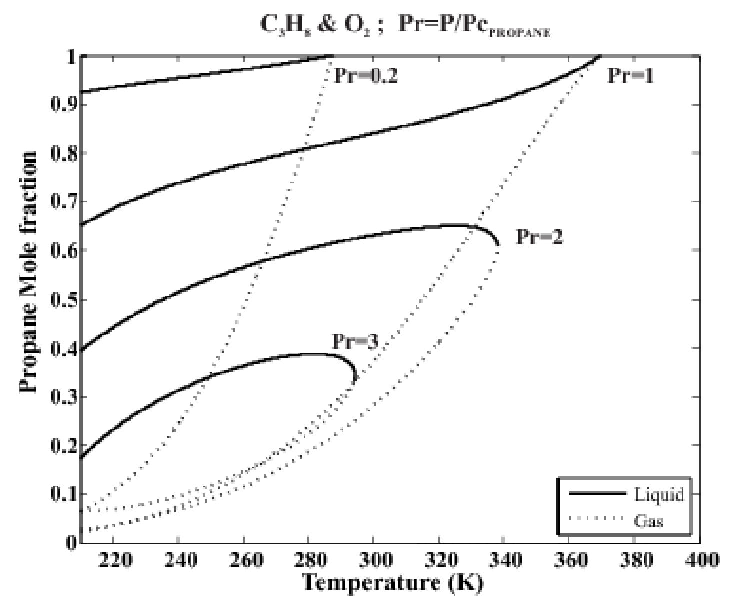
What do we mean by “high pressure”?

- *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 ?

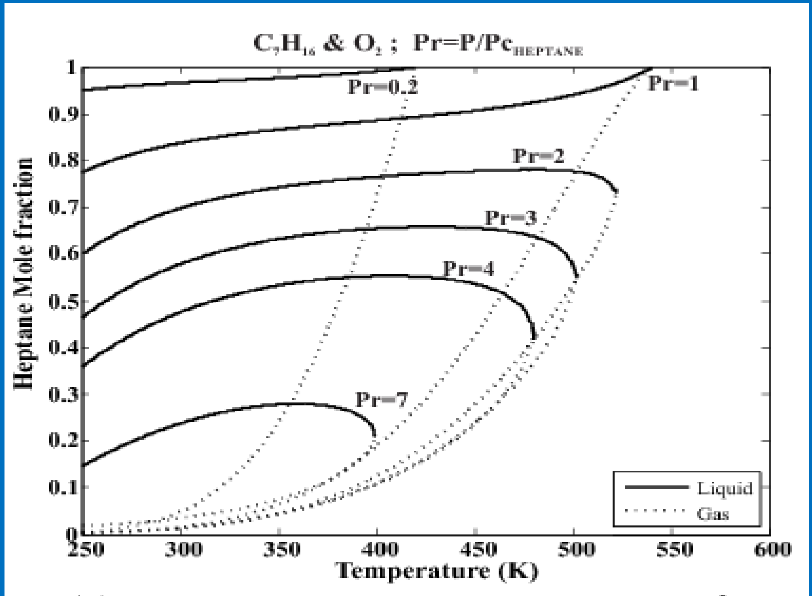
- ***It is widely and often wrongly assumed that a liquid injected into a surrounding gas at a subcritical liquid temperature but supercritical pressure for all components, may always be treated as a continuous fluid.***
- **The critical pressure of a mixture can be several times greater than the critical 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



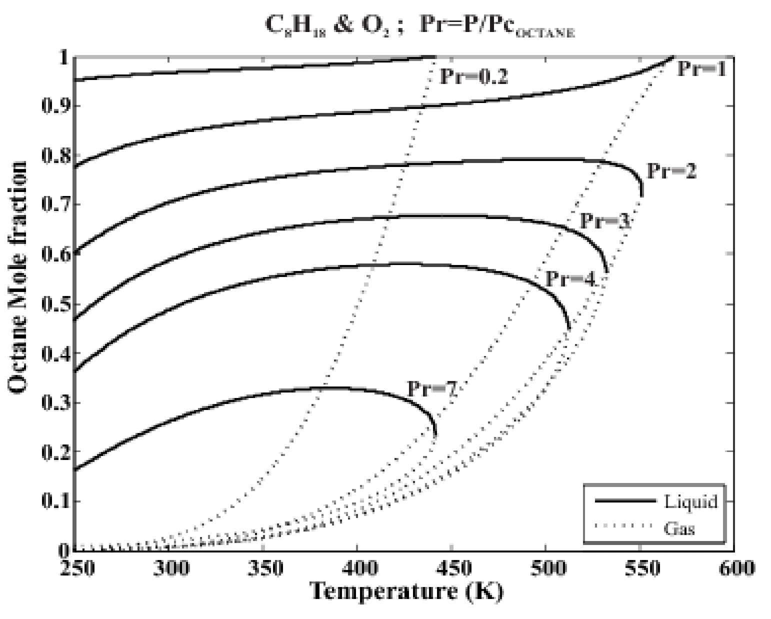
Propane
←

Heptane
→

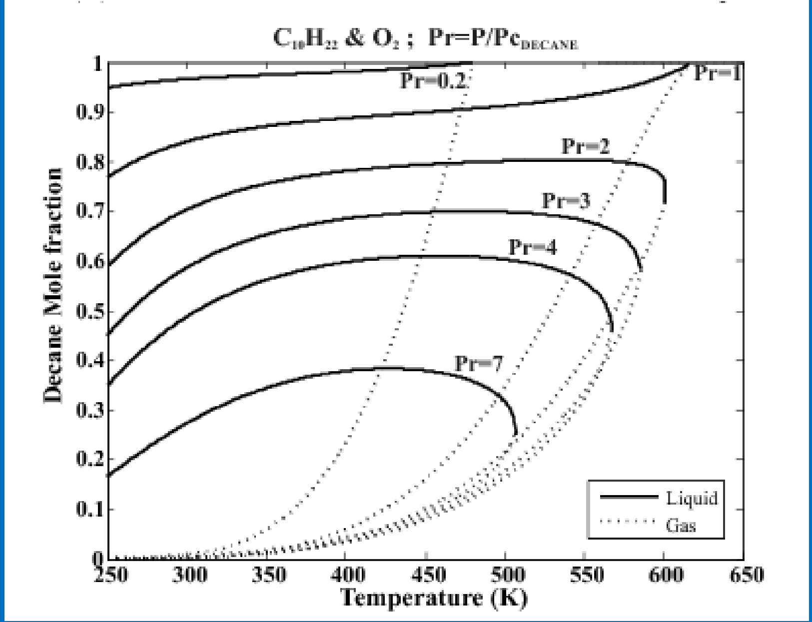


Computed by Albert Jordà Juanós

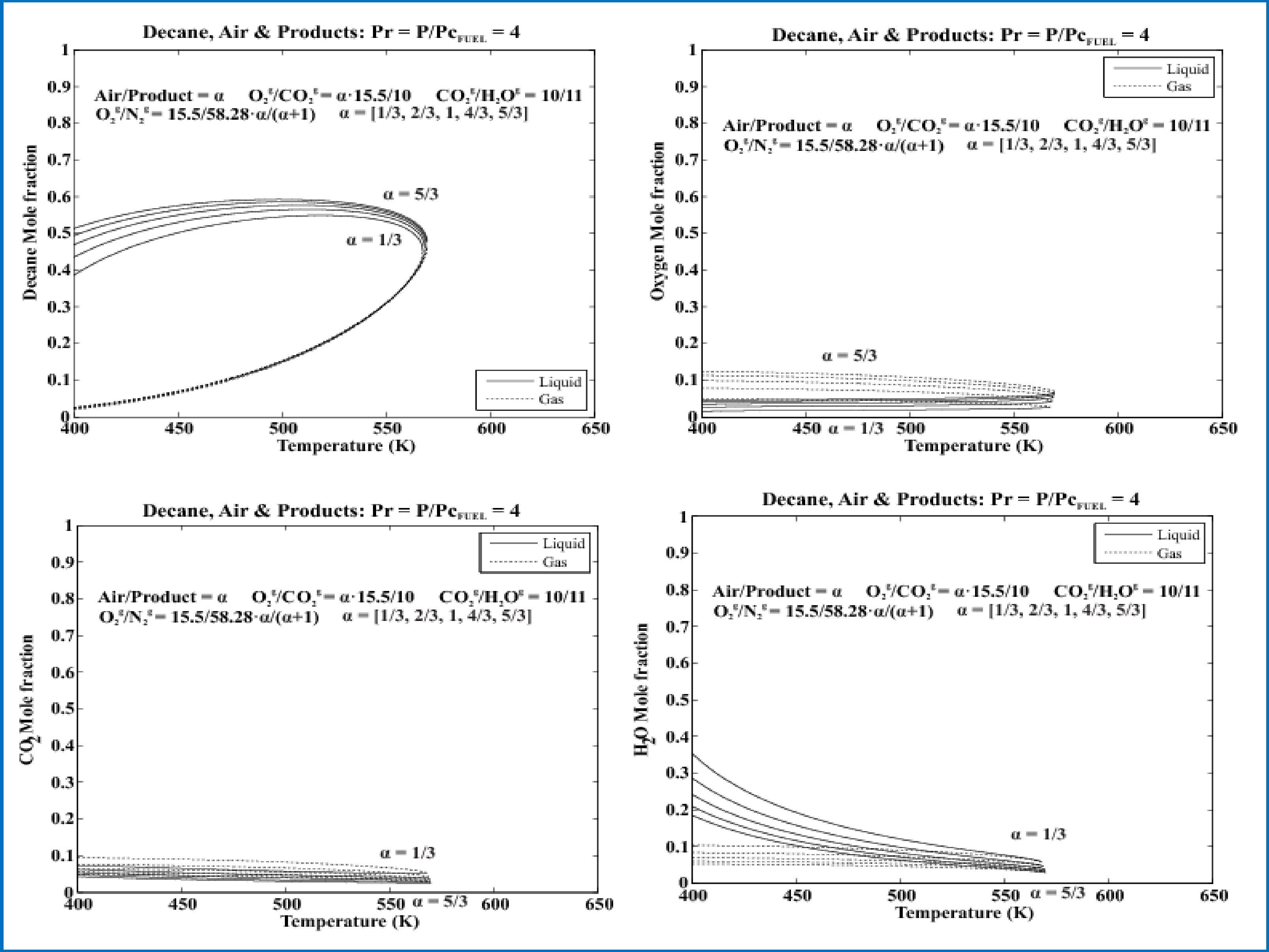
Octane
←



Decane
→



Mixture of decane, O_2, N_2, CO_2, and H_2O at 4x the critical pressure of decane. *Two phases clearly exist !!*.

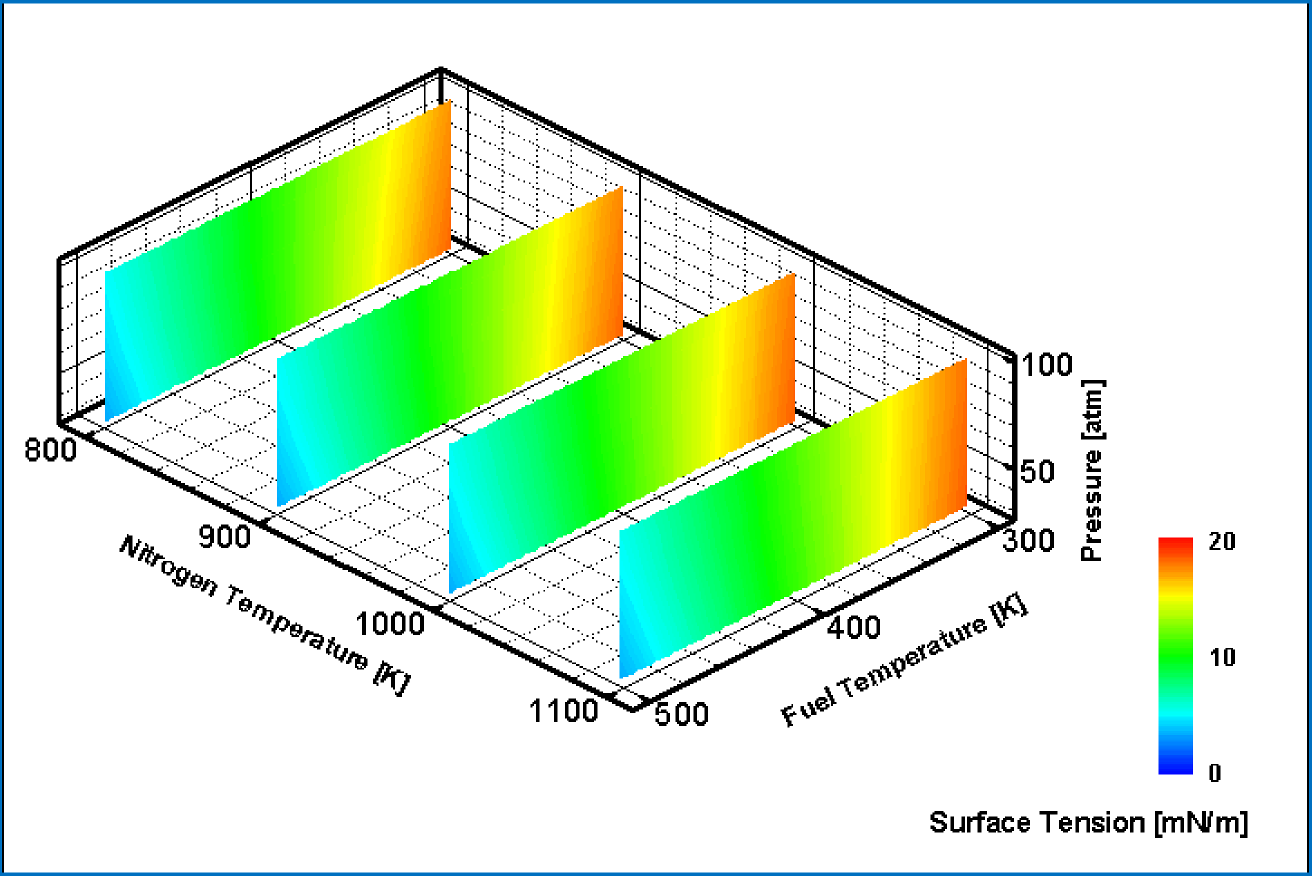


A. Jordà Juanós

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

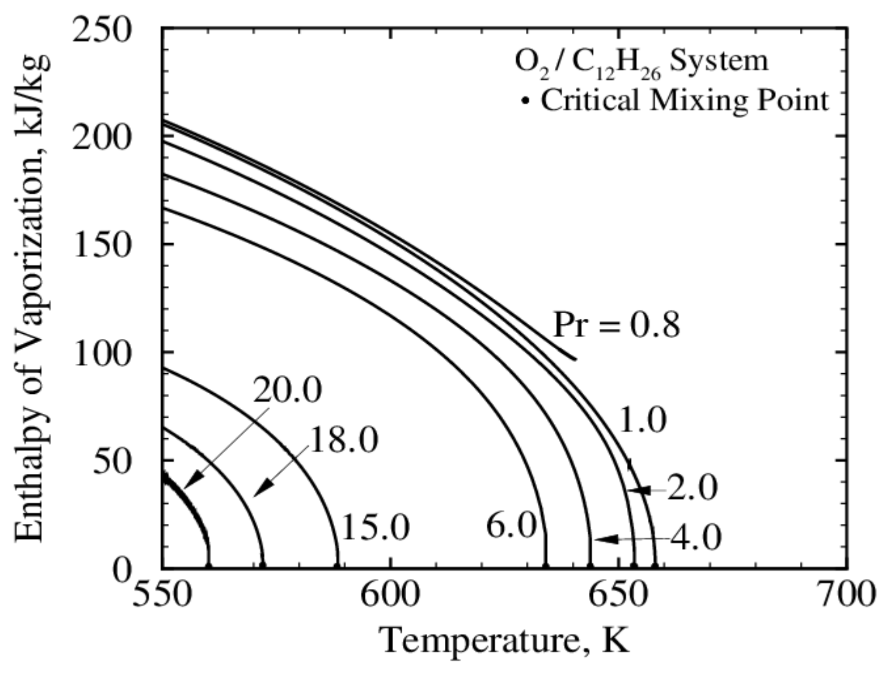


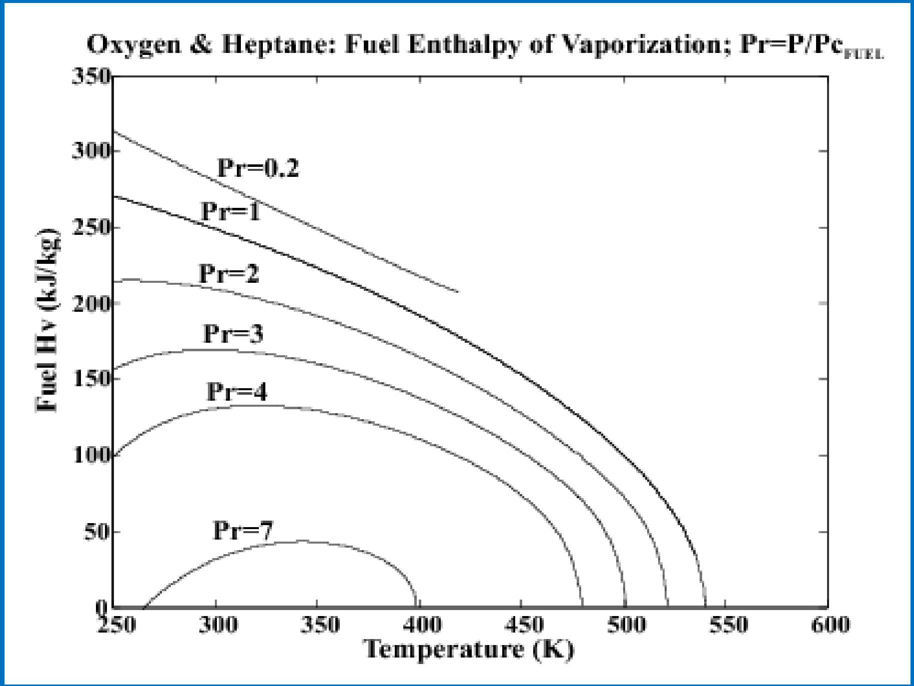
Enthalpy of Vaporization

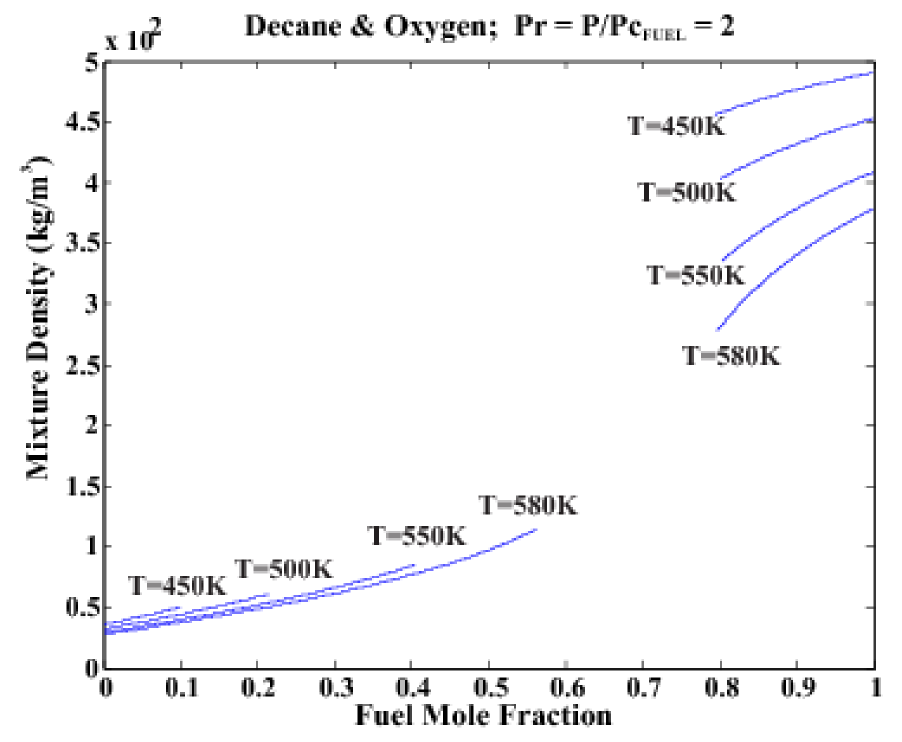
-- Latent heat of vaporization applies exactly to single species systems. Enthalpy of vaporization is needed for multispecies systems.

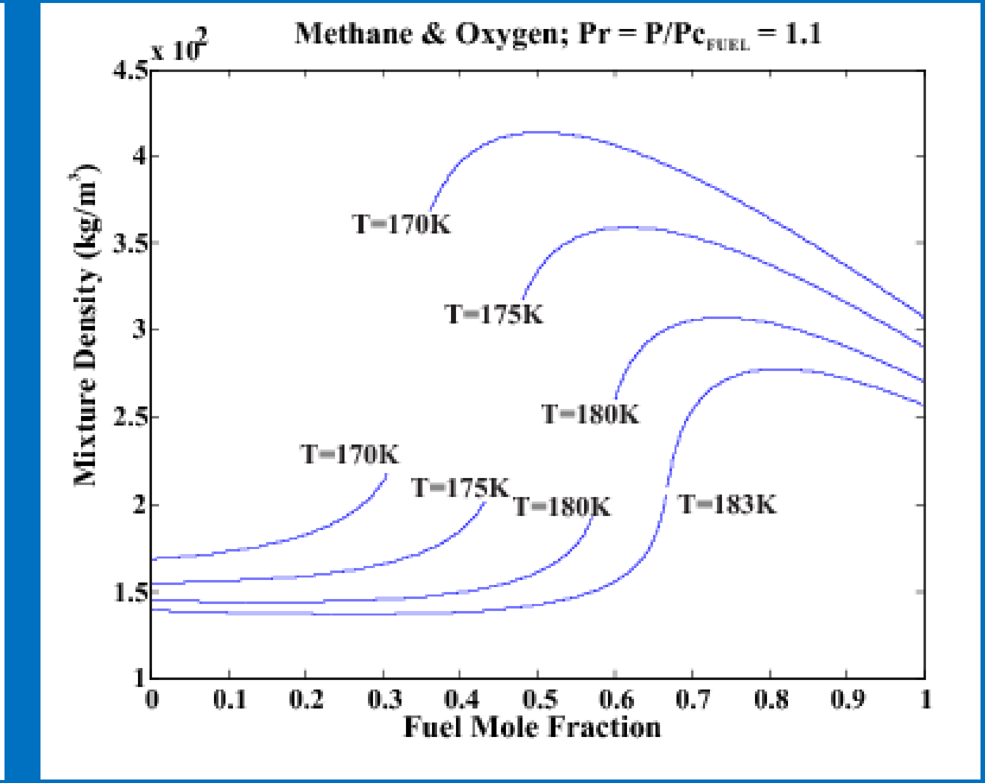
-- Enthalpy of vaporization decreases with increasing temperature and increasing pressure.

V. Yang & Co-workers *A. Jordà Juanós*









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- **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.***

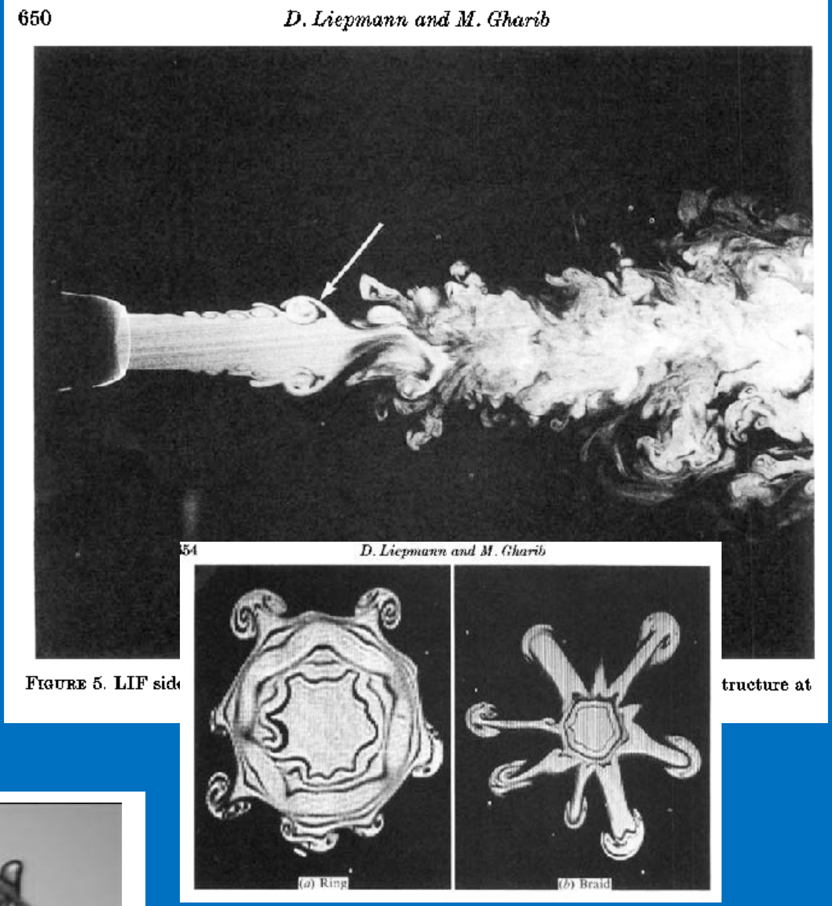
Breakup of Injected Fuel Stream
(aka atomization)
at High Reynolds and Weber numbers

- **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

Marmottant & Villermaux (2004)
Co-axial flow of liquid with air



650 *D. Liepmann and M. Gharib*

FIGURE 5. LIF sid

tructure at

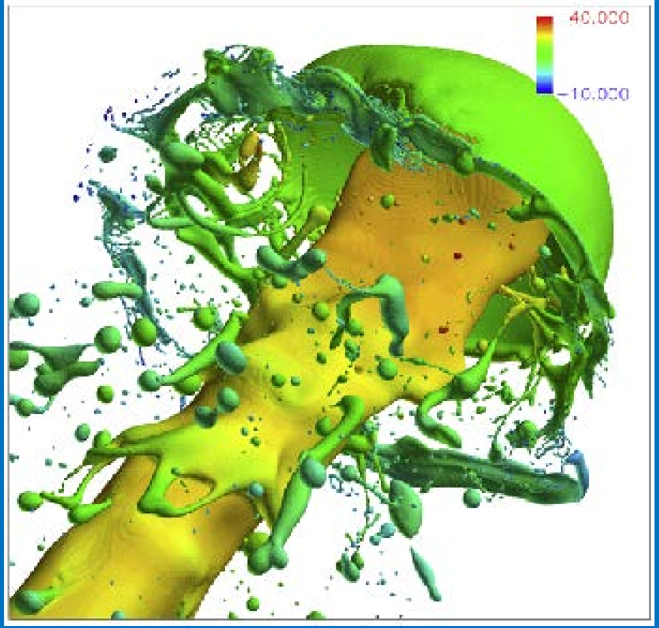
54 *D. Liepmann and M. Gharib*

(*a*) Ring

(*b*) Braid

Ring **Braid**

Vorticity analysis shows common cause between the above side jets and the ligaments and lobes to the left.

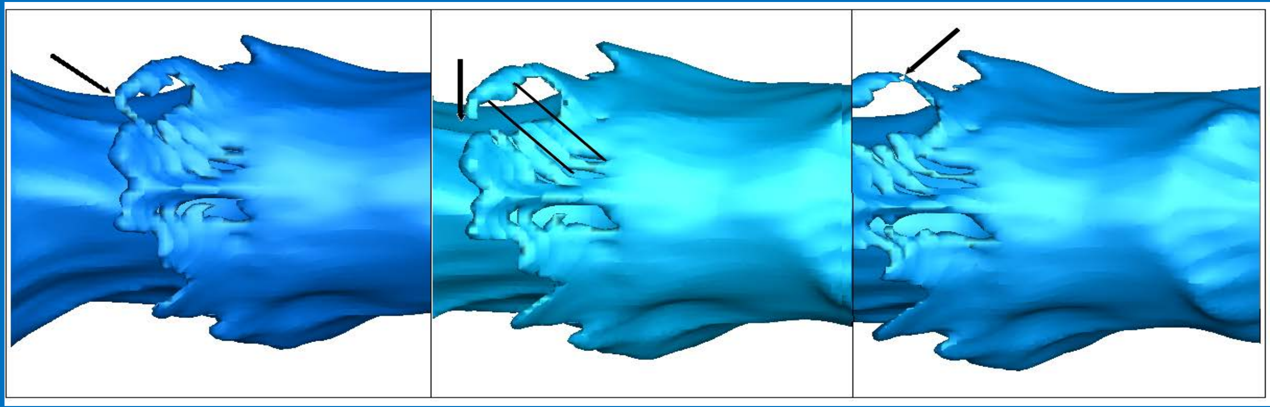


Liquid transient, round jet into still air

Shinjo & Umemura (2010), NS-LS
Re = 440 – 1470; We = 1270 – 14,100

Jarrahbashi & Sirignano (2014), NS-LS-PP
Re = 1600 ; We = 230000 ; ρ_1 / ρ_2 = 0.1

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



time →

-- Cones have azimuthal instability. Lobes form.
-- Lobes stretch and tear under azimuthal instability.
-- Ligaments form from torn rims.
-- Capillary instabilities on ligaments.

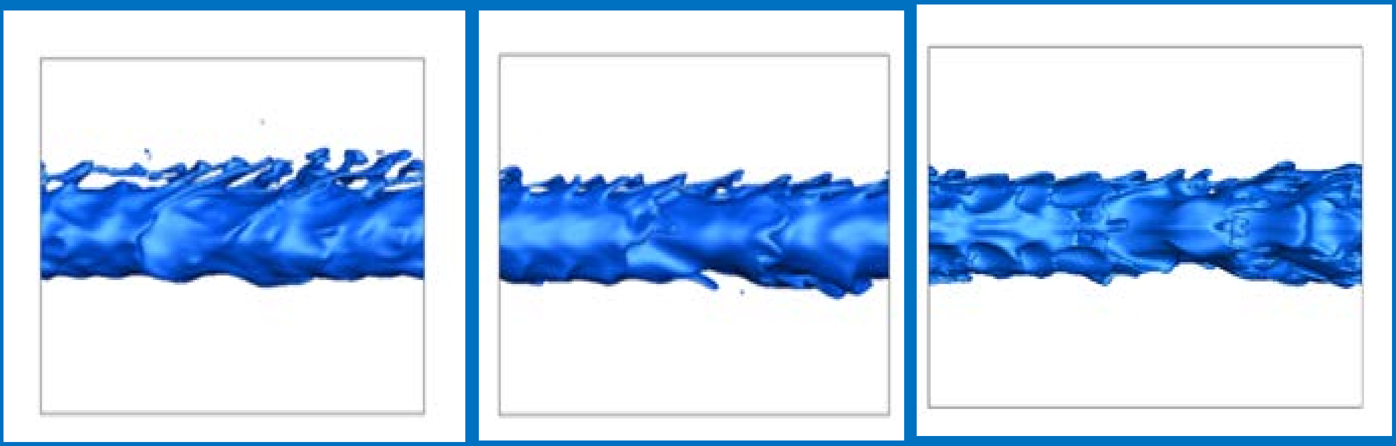
Density ratio affects 3D instability but a qualitative similarity exists over a wide range. *There is no basis for assuming large qualitative distinction in cone, lobe, and ligament formations for supercritical injection at low Mach numbers.*

$Re = 1600$

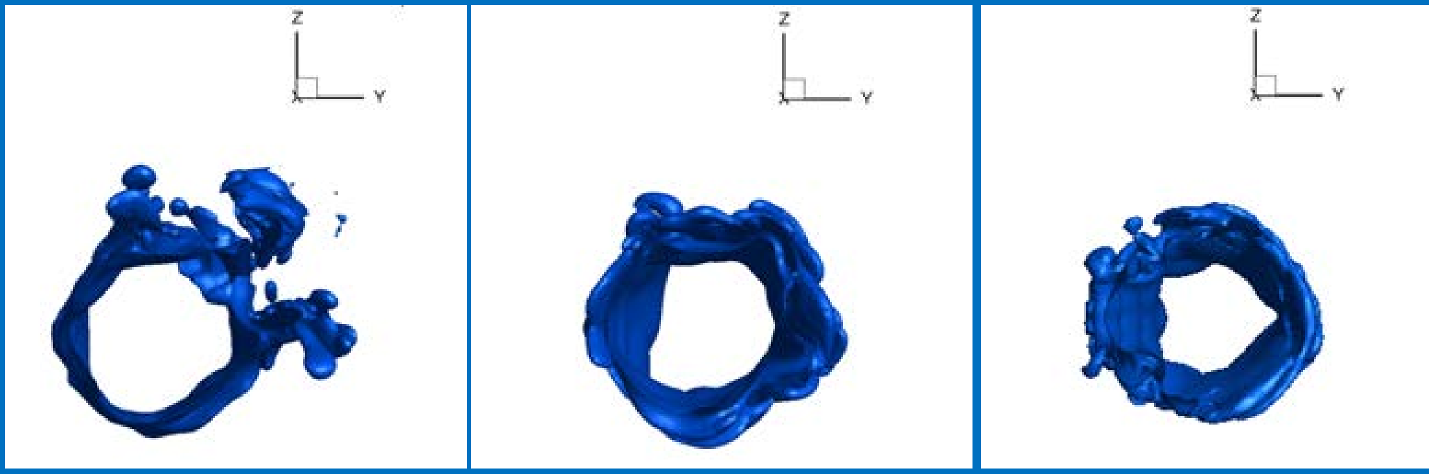
$We = 230{,}000$

$\mu_1 / \mu_2 = 9 \times 10^{-4}$

$t = 90\ \mu s$



$\rho_1 / \rho_2 =$ 0.1 , 0.5 , 0.9



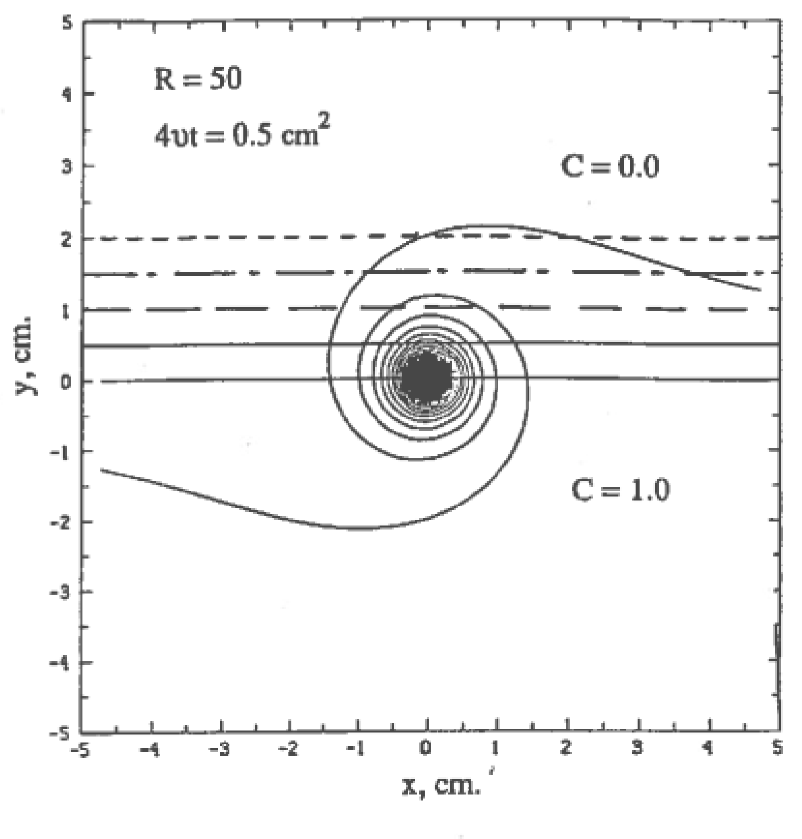
Turbulent Mixing

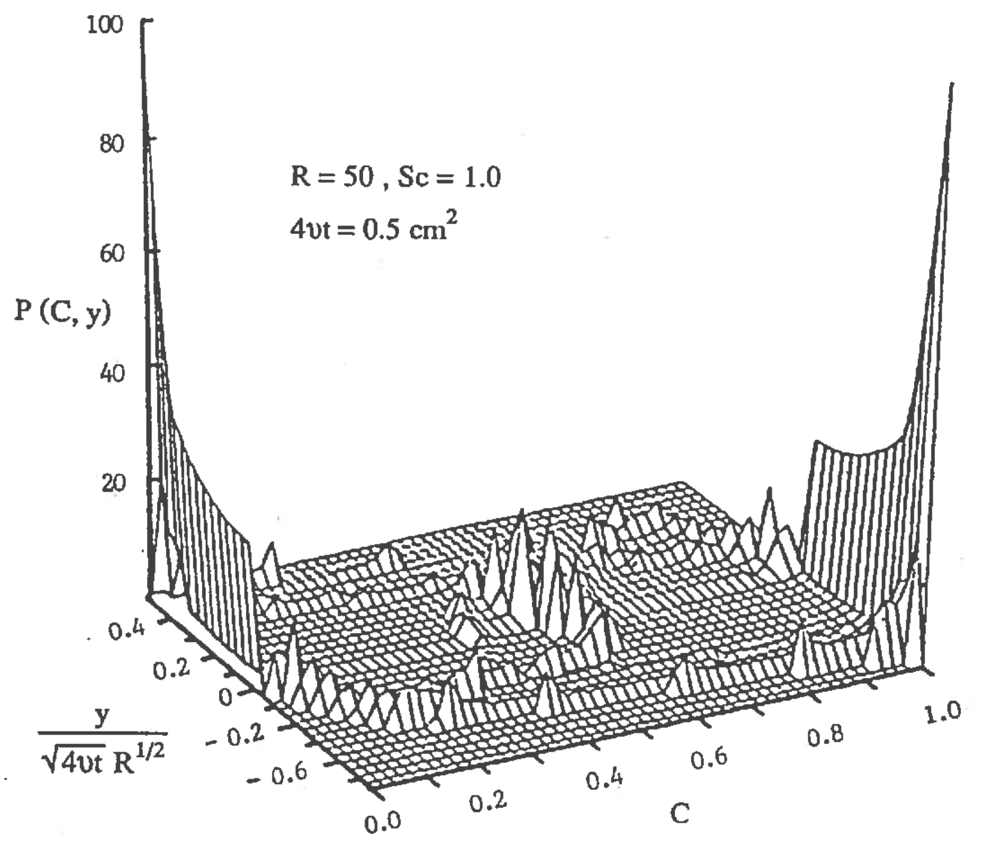
- ***Molecular transport remains important even with turbulent eddies enhancing mixing.***
- **Simple models developed first by Marble (1985), Karagozian & Marble (1986), Cetegen & Sirignano (1989, 1990) explain how molecular mixing and reaction occur in the strained flow within an eddy.**
- **The temporal 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: $f(t) = \langle C_1 C_2 \rangle / [\langle C_1 \rangle \langle C_2 \rangle]$ where C_1 and C_2 are concentrations and < > implies an instantaneous volume average. With complete mixing f =1; with no mixing, f =0.**

Two-dimensional Eddy Mixing, Cetegen & Sirignano

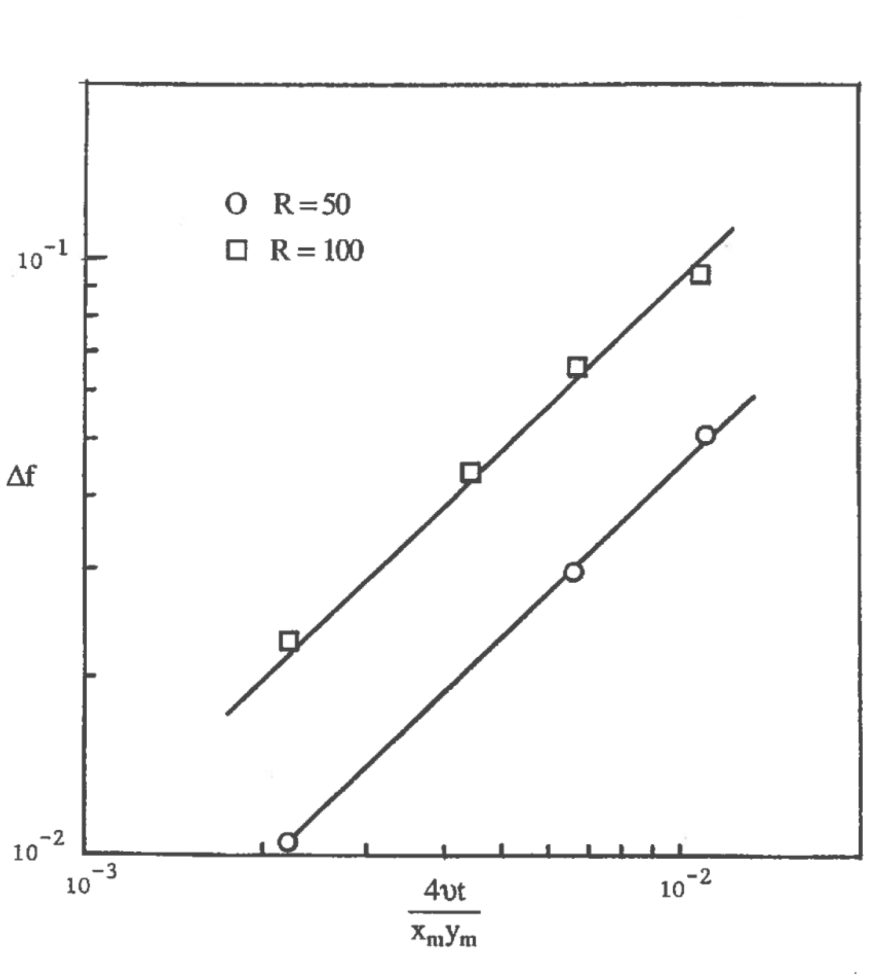
Sc = 1, (D = υ) ; R = Γ/ υ

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

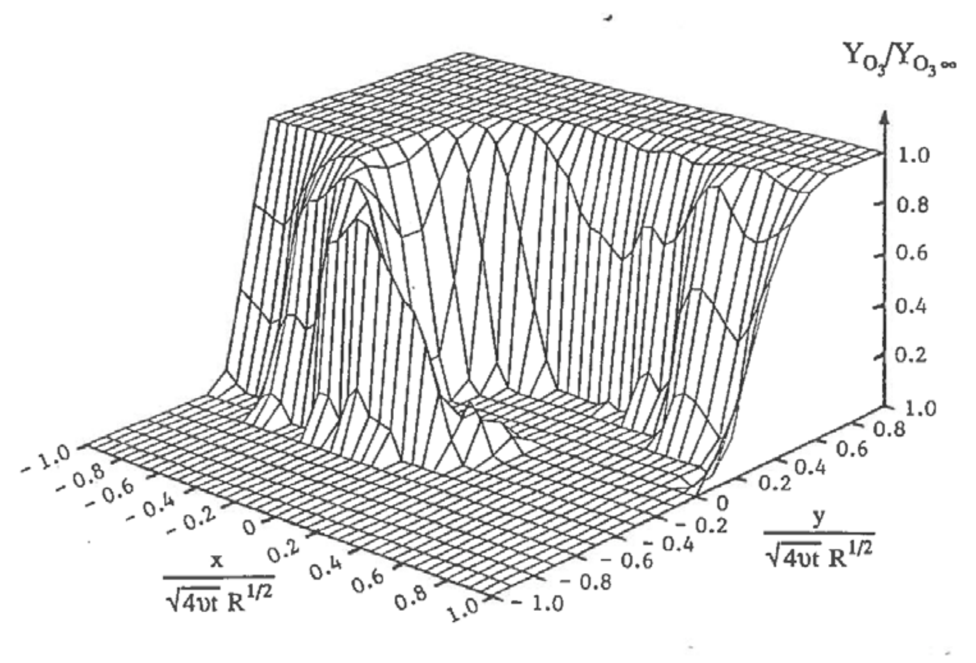


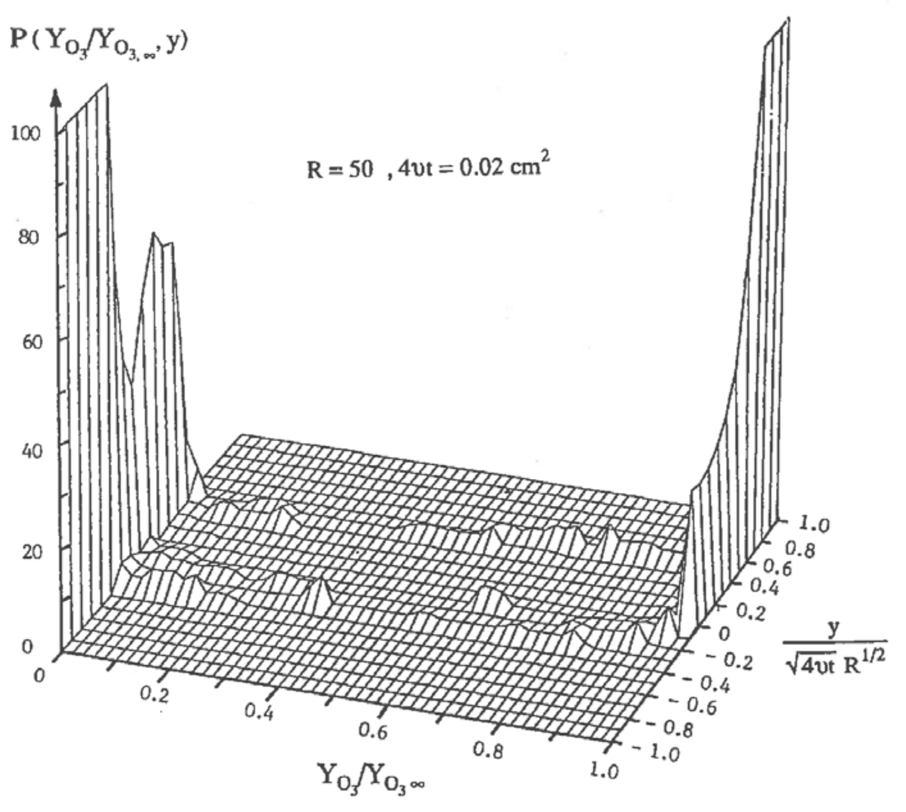
Mixedness enhancement Δf due to eddy circulation and strain increases with time, vortex strength, and mass diffusivity.

$D = \upsilon$; $R = \Gamma/\ \upsilon$

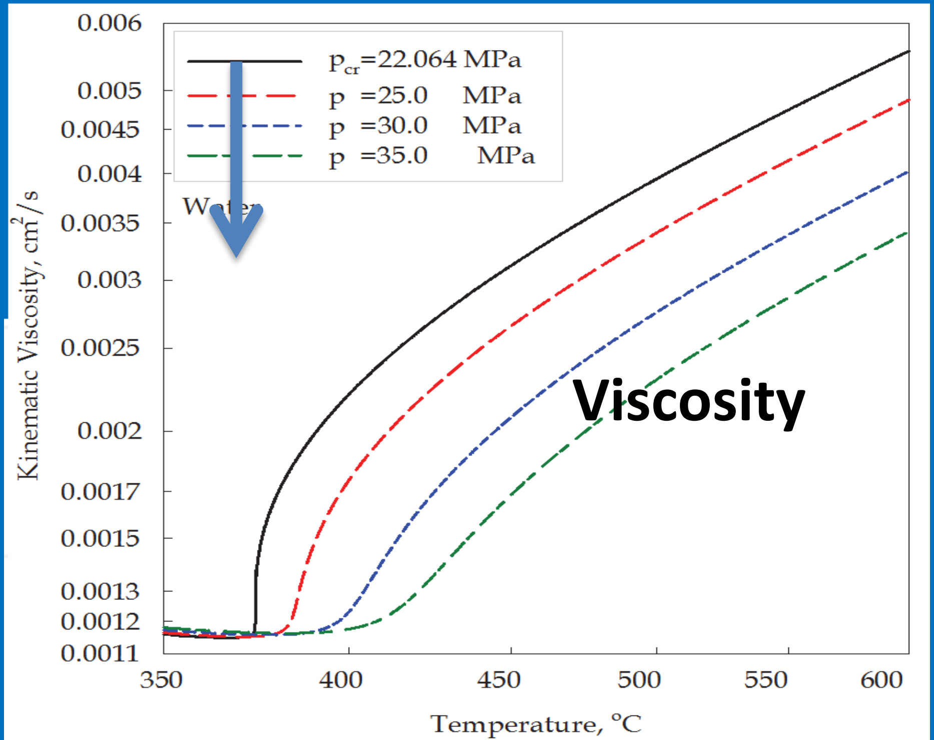
Turbulent Mixing of O_3 and NO with isothermal chemical reaction

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

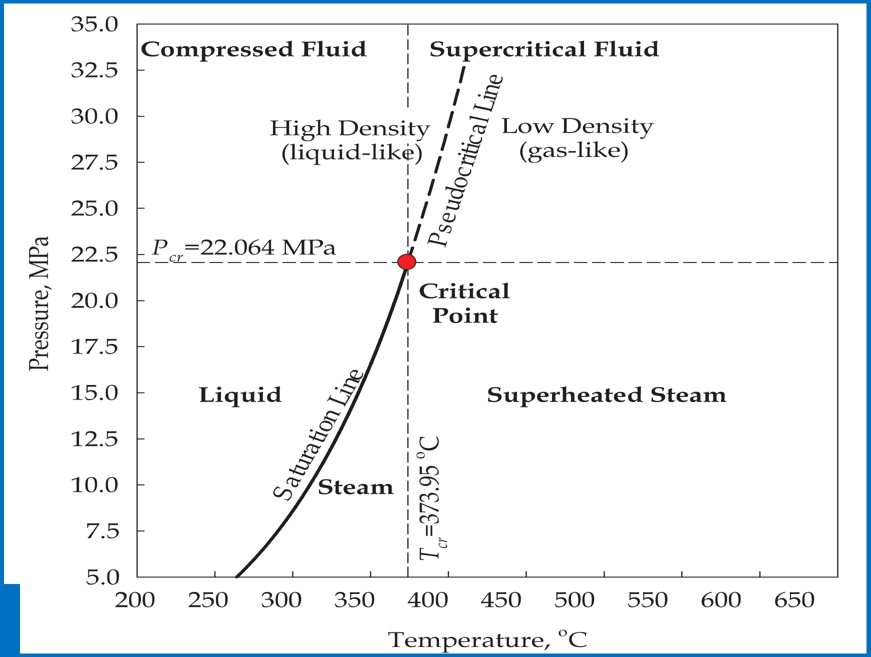


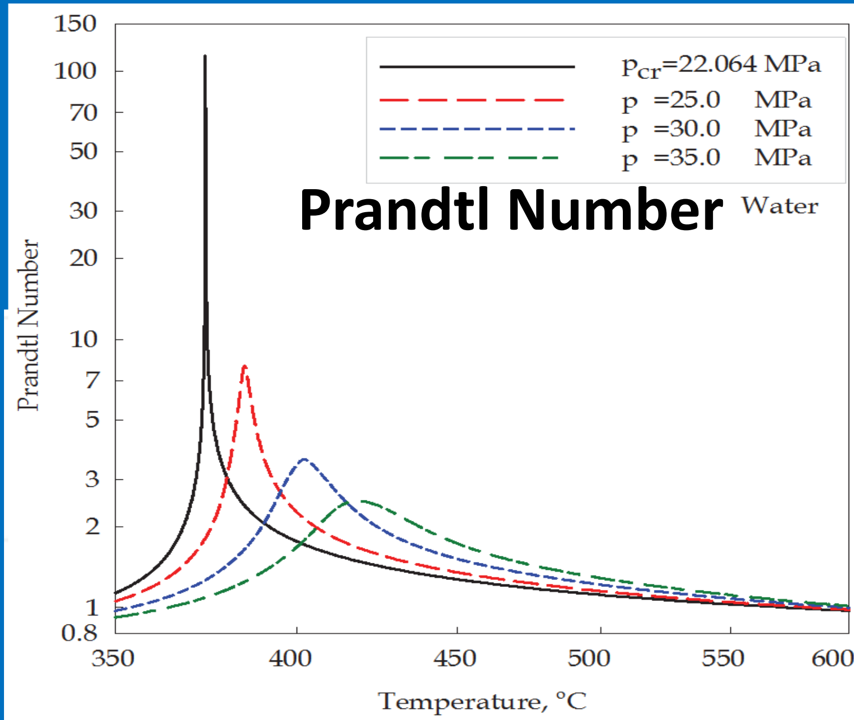


Molecular Transport



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.

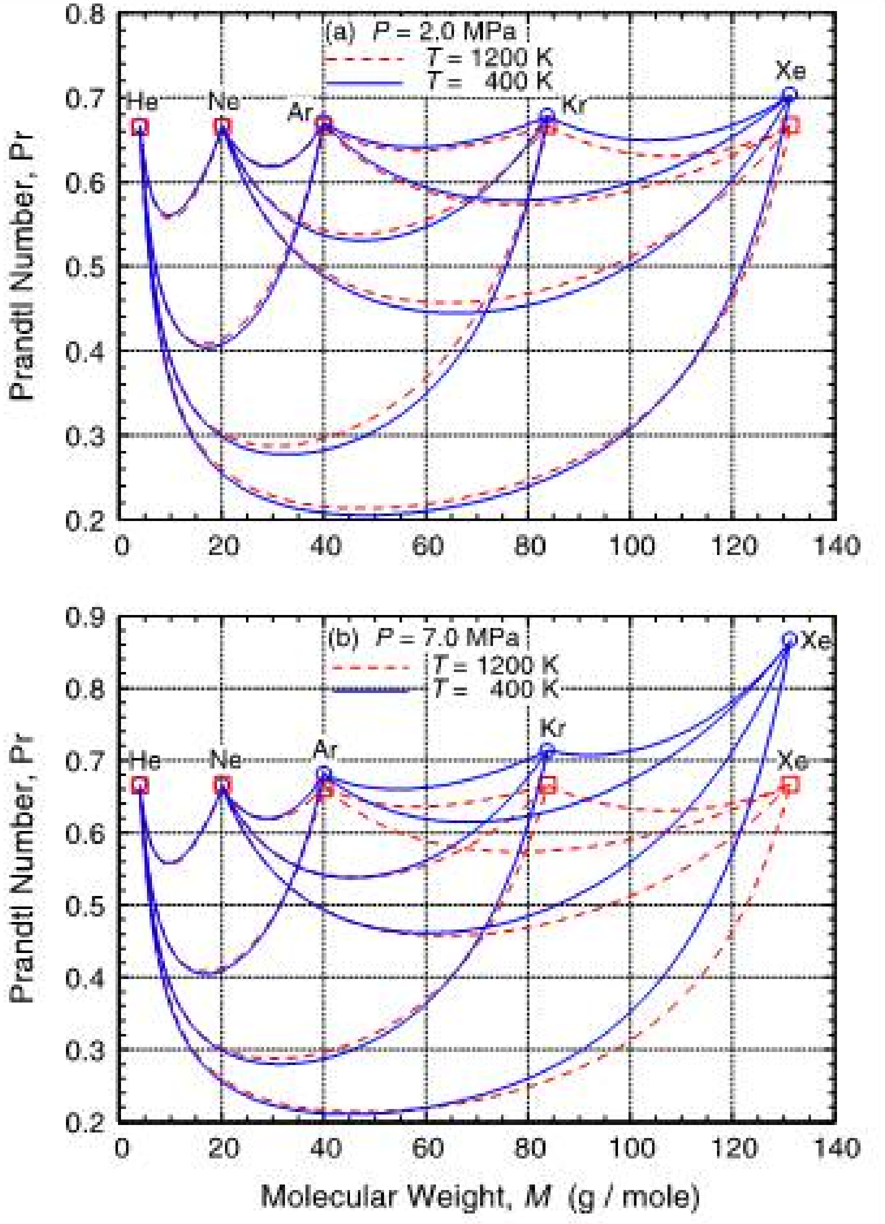


Fig. 35. Prandtl number of noble gases and their binary mixtures at pressures of 2 and 7 MPa.

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.**

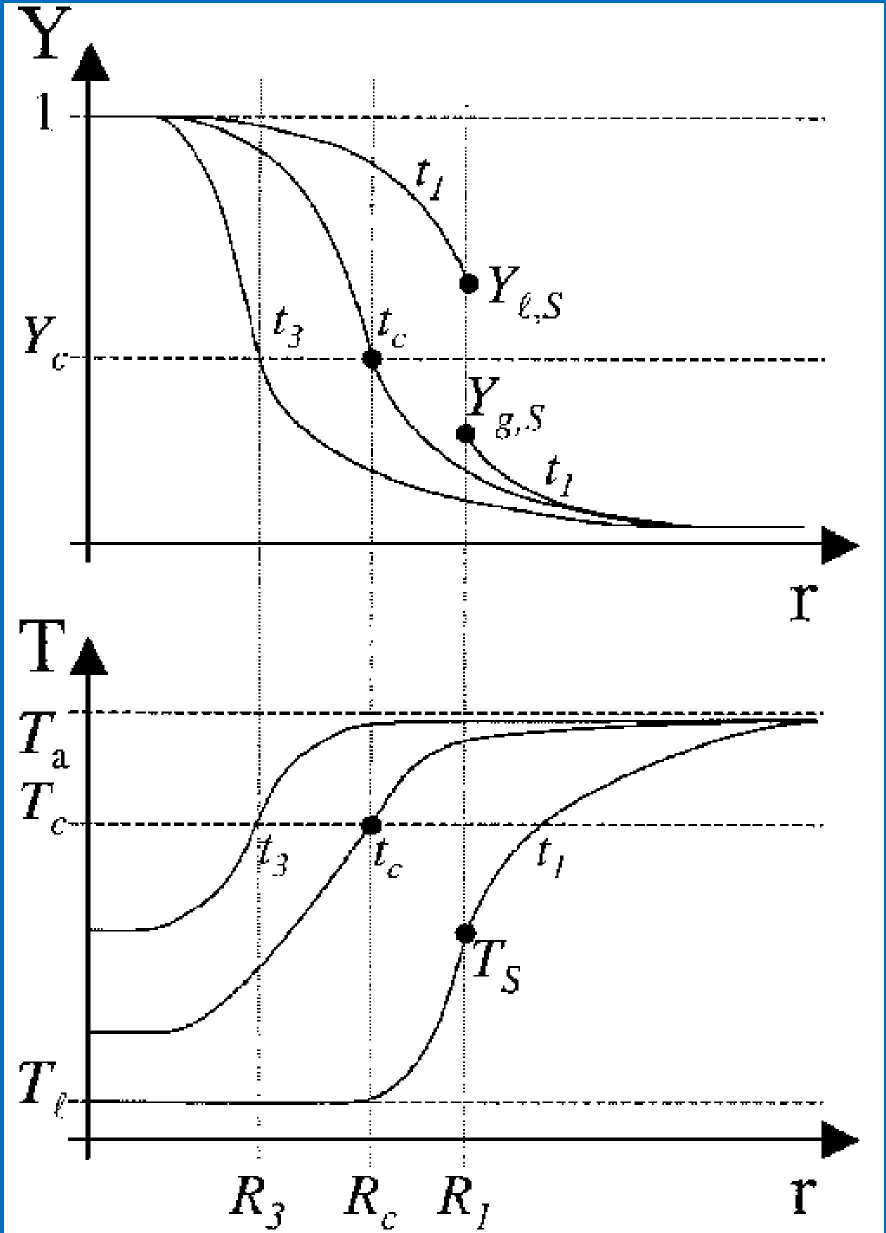
Vaporization

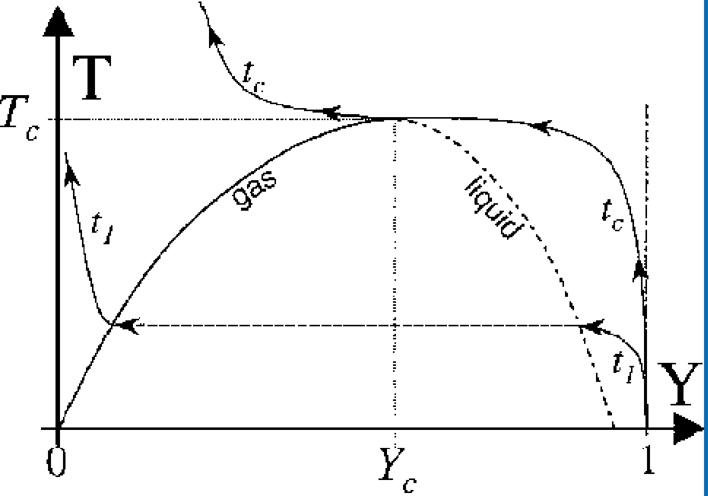
A cold fuel droplet might be sub-critical for its local gas mixture.

--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