

Ayyaswamy Symposium

**Unsteady Transport at a Liquid-Gas Interface
at Supercritical Pressure**

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**From the MS Thesis of Jordi Poblador-Ibanez and
the PhD dissertations of Dorrin Jarrahbashi and
Arash Zandian**

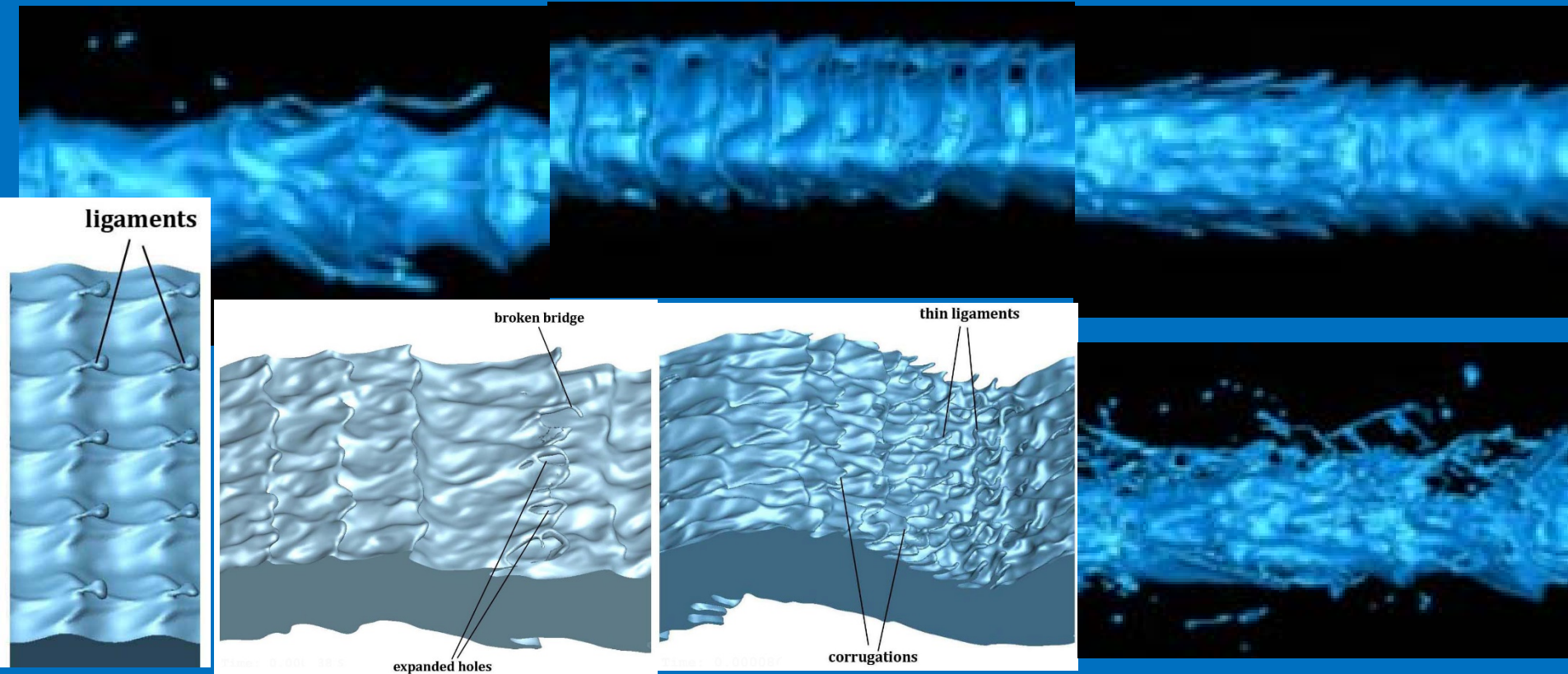
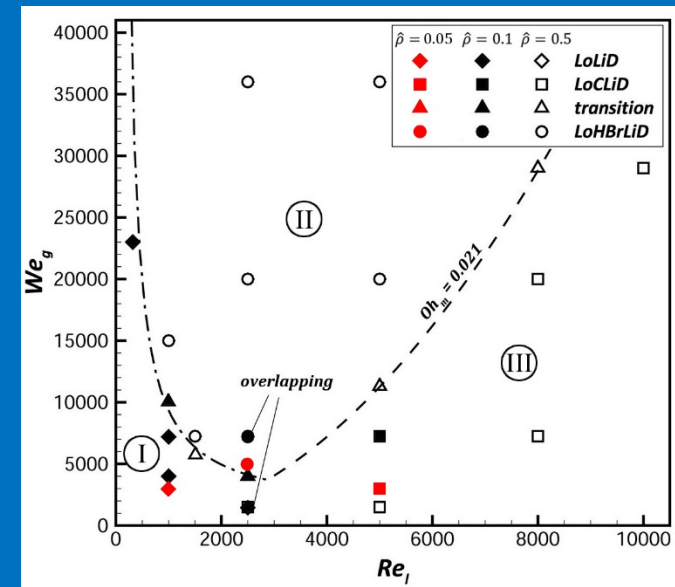
**At very high pressures and densities,
what is different and what is similar
about Atomization and Phase Change**

Three Domains of Atomization for Incompressible Fluid

Domain I: Lobe –Ligament-Droplet

Domain II: Lobe-Hole-Bridge-
Ligament-Droplet

Domain III: Lobe-Corrugation-
Ligament-Droplet



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

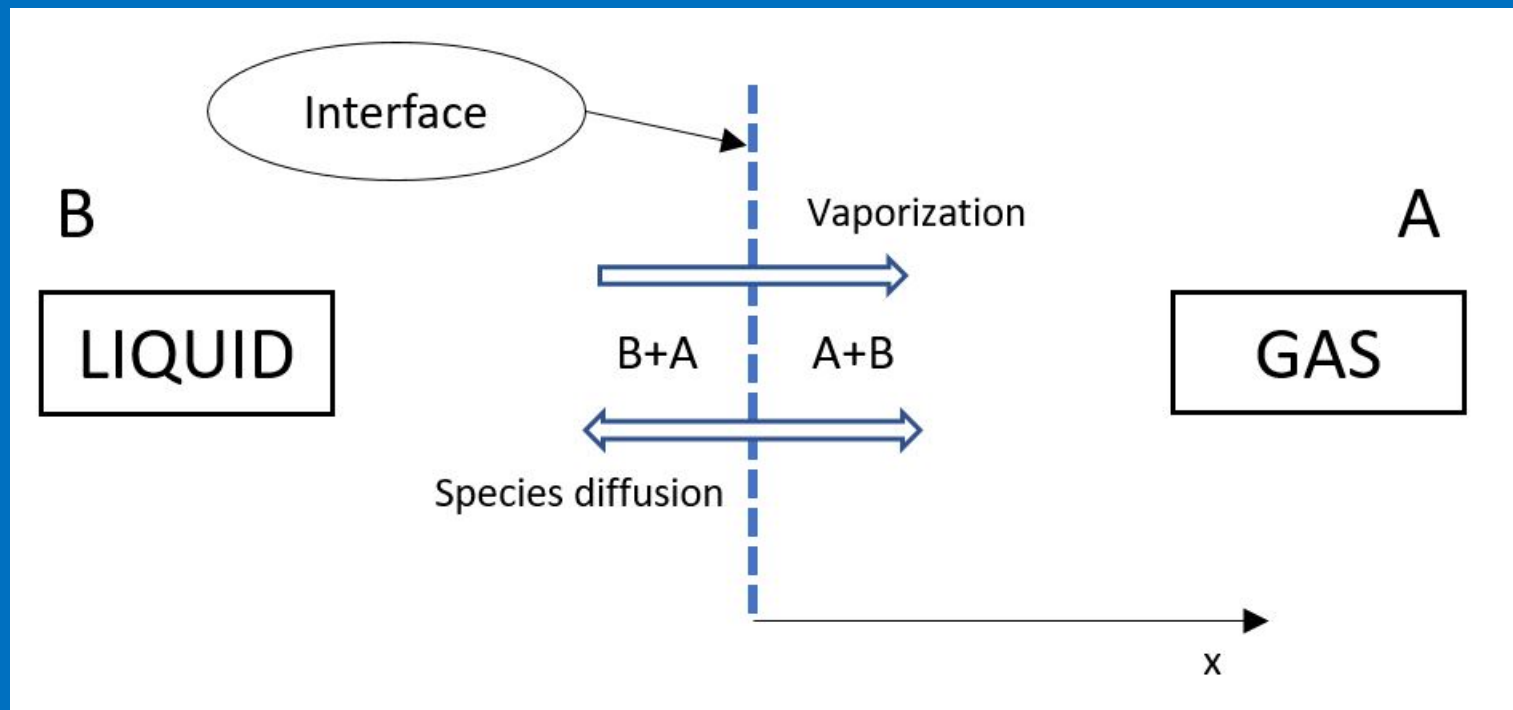
- The disintegration of the injected fuel stream determines the chamber mixture ratio distribution and the length scales for the resulting fuel droplets, ligaments, or ‘blobs’ thereby affecting rate controlling processes such as vaporization and mixing.
- *Thus, without knowledge of these processes, we have no starting point for practical combustion analysis.*
- Except for final stages in the cascade, the atomization process is weakly dependent on surface tension.
- Consequently, substantial similarities are found for homogeneous jets (e.g., air-into-air or water-into-water) and liquid jets into gas. Vorticity dynamics explains the cascade which is essentially a turbulent transition process with hairpin vortices playing key roles.

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, Redlich-Kwong, or Soave-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.

One-Dimensional Unsteady Formulation

Hydrocarbon liquid (octane or decane) and hotter gas (nitrogen or oxygen) are introduced initially at an interface. Pressure is constant and uniform.



At high pressures, gas dissolves quickly in liquid and some vaporization occurs. Critical pressure values of solution and mixture are higher than component critical values.

Continuity and Energy Equations

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) = 0$$

$$\rho \frac{\partial Y_i}{\partial t} + \rho u \frac{\partial Y_i}{\partial x} + \frac{\partial}{\partial x}(J_i) = 0$$

$$\rho \frac{\partial h}{\partial t} + \rho u \frac{\partial h}{\partial x} - \rho \sum_{i=1}^N h_i \frac{\partial Y_i}{\partial t} - \rho u \sum_{i=1}^N h_i \frac{\partial Y_i}{\partial x} - \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + \sum_{i=1}^N J_i \frac{\partial h_i}{\partial x} = 0$$

State Equations for Density, Enthalpy, and Entropy

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$Z = \frac{pv}{R_v T} \quad ; \quad A = \frac{ap}{(R_v T)^2} \quad ; \quad B = \frac{bp}{R_v T}$$

$$a = \sum_{i=1}^N \sum_{j=1}^N X_i X_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad ; \quad b = \sum_{i=1}^N X_i b_i$$

$$a_i = 0.42748 \frac{(R_v T_{ci})^2}{p_{ci}} \alpha_i \quad ; \quad b_i = 0.08664 \frac{R_v T_{ci}}{p_{ci}}$$

$$\alpha_i = [1 + S_i (1 - T_{ri}^{0.5})]^2 \quad ; \quad S_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2$$

$$h = h^*(T) + \frac{1}{MW} \left[R_v T (Z - 1) + \frac{T (\partial a / \partial T) |_{p, X_i} - a}{b} \ln \left(\frac{Z + B}{Z} \right) \right]$$

$$s = s^*(T) + \frac{1}{MW} \left[\frac{1}{b} \left(\frac{\partial a}{\partial T} \right) |_{p, X_i} \ln \left(\frac{Z + B}{Z} \right) + R_v \ln(Z - B) \right]$$

Interface Conditions:

Phase Equilibrium and Conservation Laws

$$p_l = p_g$$

$$T_l = T_g$$

$$f_{li} = f_{gi}$$

$$\Phi_i = \frac{f_i}{p_i} = \frac{f_i}{pX_i}$$

$$X_{li}\Phi_{li} = X_{gi}\Phi_{gi}$$

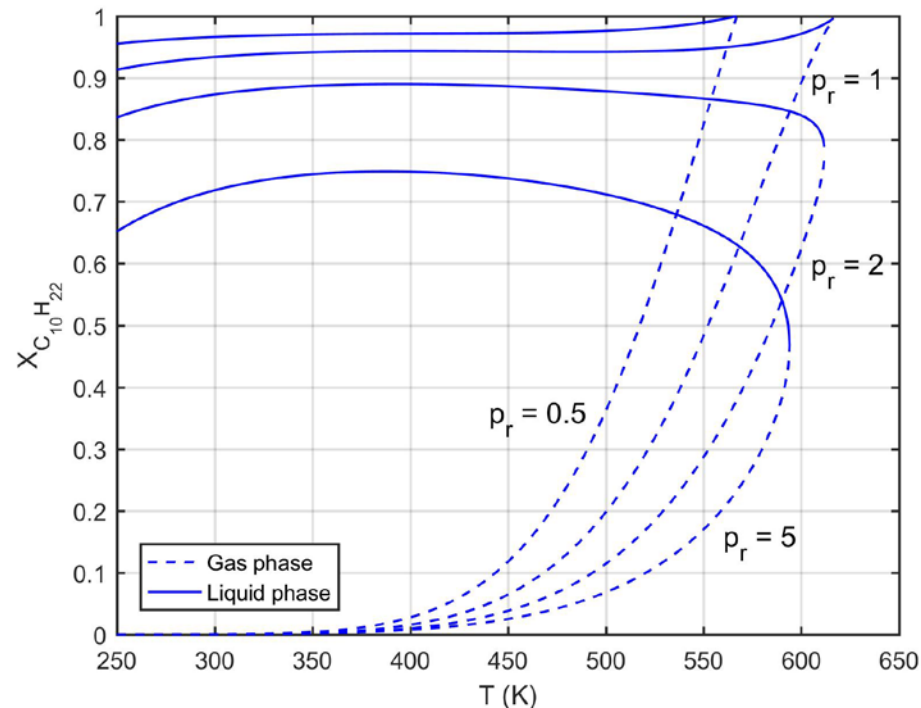
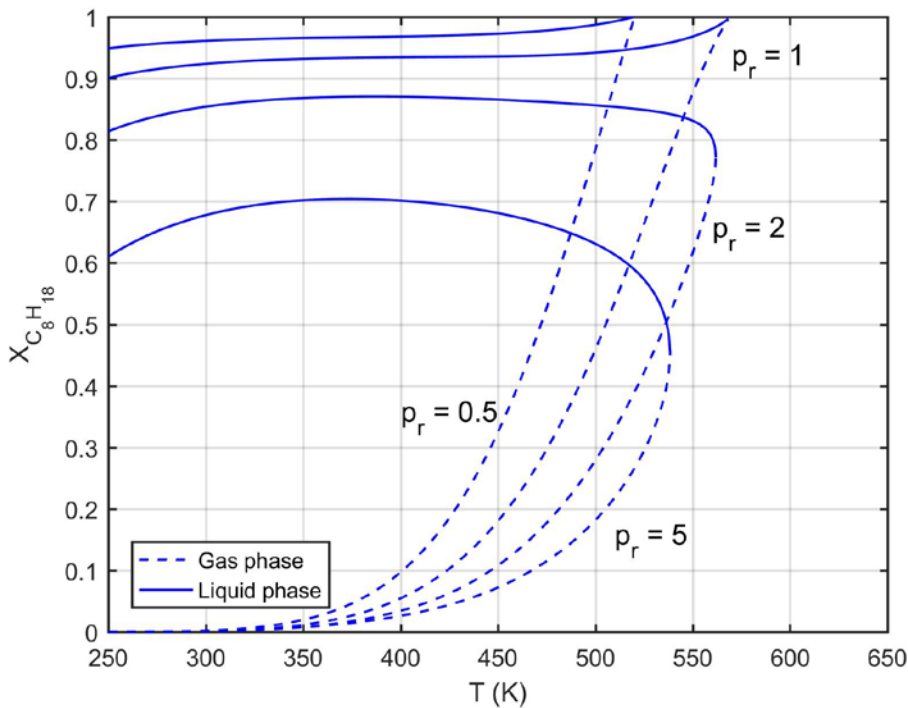
$$\ln(\Phi_i) = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{B} \left[2 \left(\frac{a_i}{a} \right)^{0.5} - \frac{b_i}{b} \right] \ln \left(1 + \frac{B}{Z} \right)$$

$$\rho_g Y_{gi}(u_g - U) + J_{gi} = \rho_l Y_{li}(u_l - U) + J_{li}$$

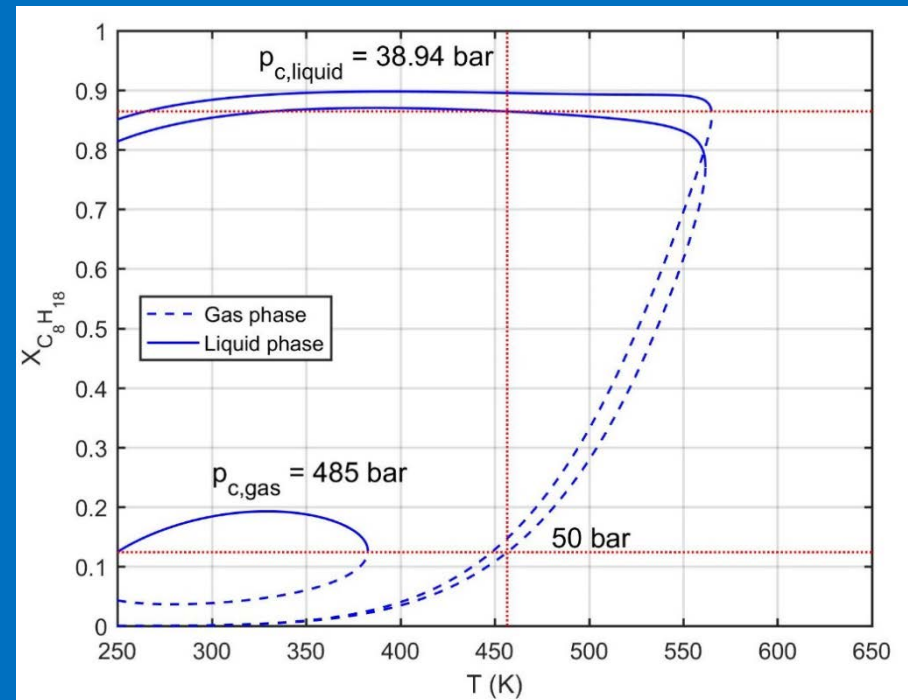
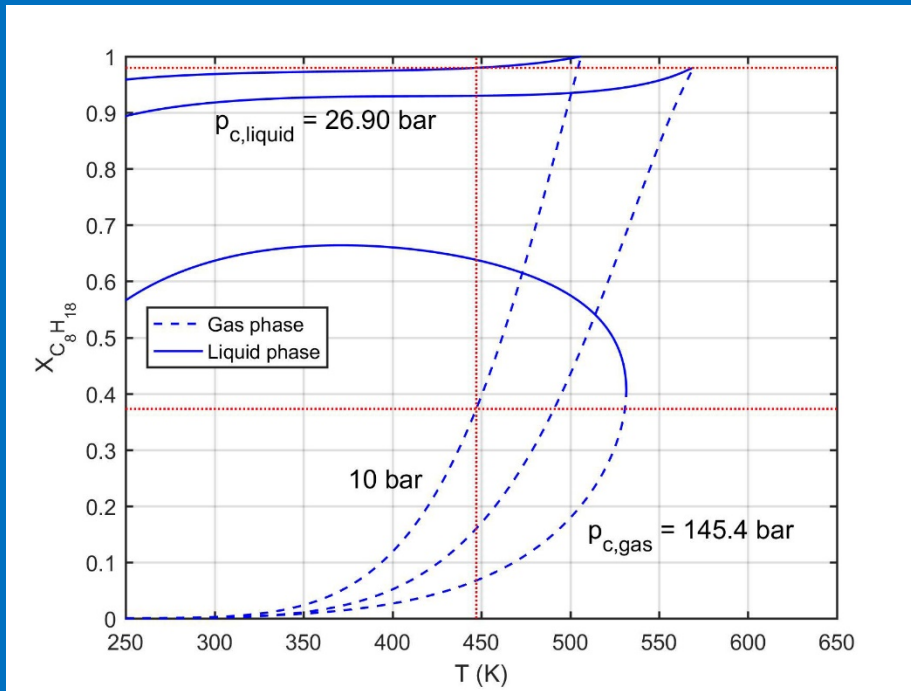
$$\rho_l u_l h_l - \lambda_l \frac{\partial T}{\partial x} + \sum_{i=1}^N J_{li} h_{li} - \rho_l U h_l = \rho_g u_g h_g - \lambda_g \frac{\partial T}{\partial x} + \sum_{i=1}^N J_{gi} h_{gi} - \rho_g U h_g$$

Phase Equilibrium

The critical pressure of a mixture can be several times greater than the critical values for the components. Near the critical point, gas more easily dissolves in liquid and liquid more easily vaporizes; surface tension and energy of vaporization are reduced but can still exist. Both phases must be considered as mixtures (or solution).

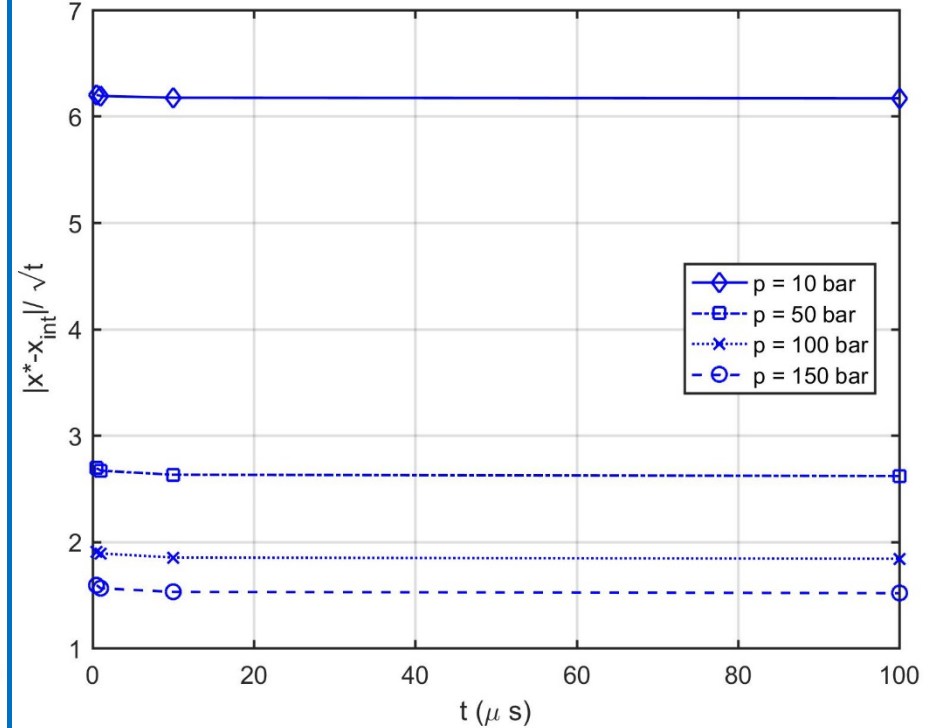
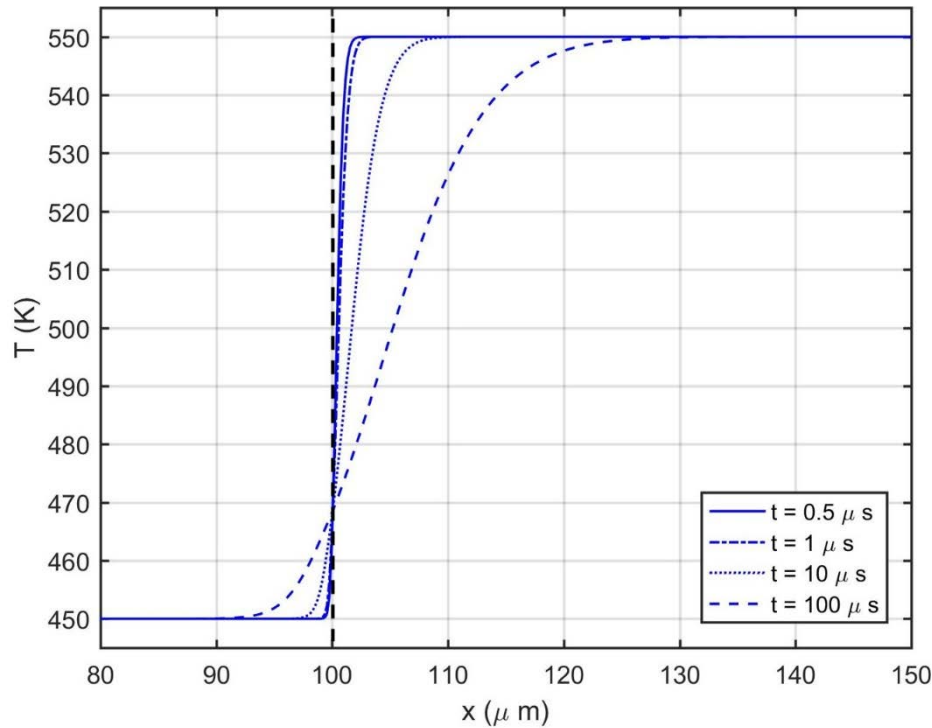


Octane – Oxygen at 10 Bar and 50 Bar



- Composition, critical pressure and critical temperature are discontinuous across the phase interface .
- At 10 bar, liquid and gas have sub-critical pressure and sub-critical temperature.
- At 50 bar, the liquid has supercritical pressure and sub-critical temperature while the gas has subcritical pressure and supercritical temperature.

Diffusion Control – Oxygen and Decane



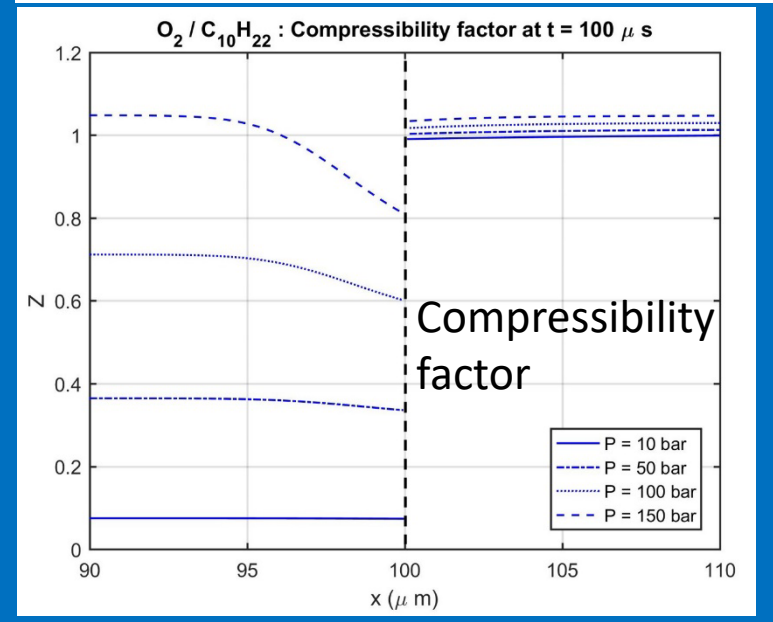
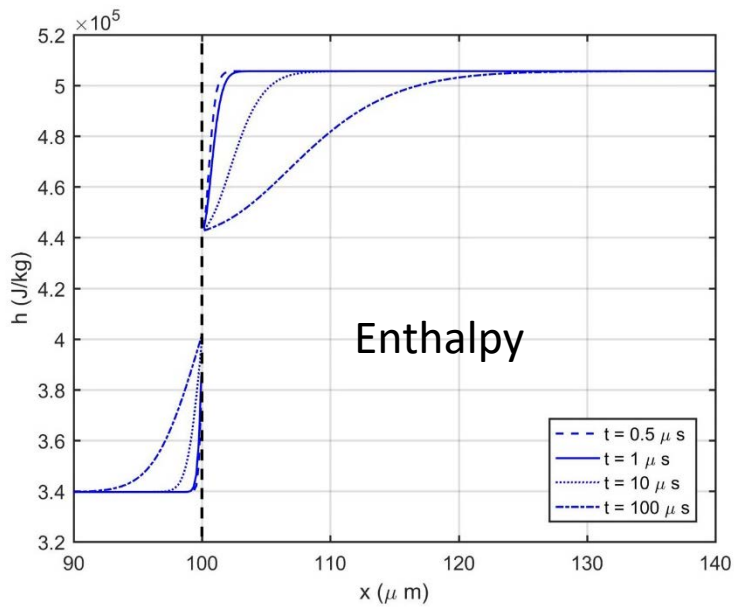
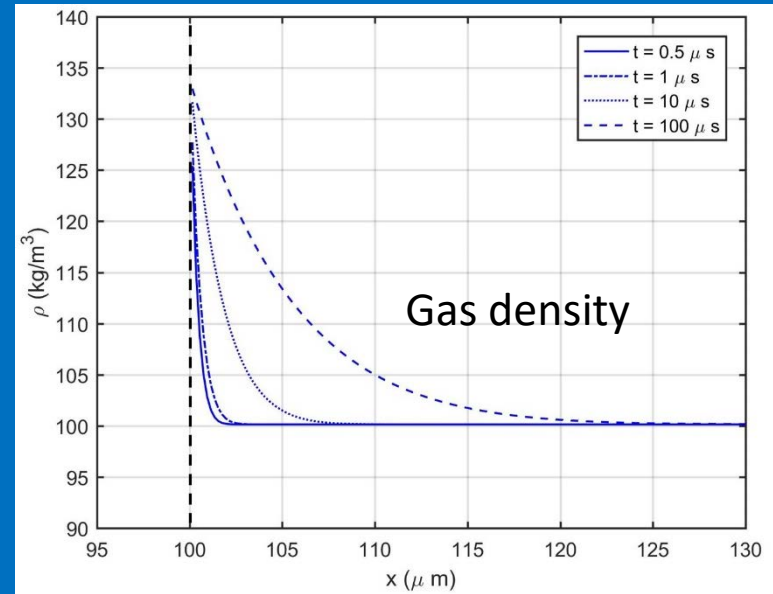
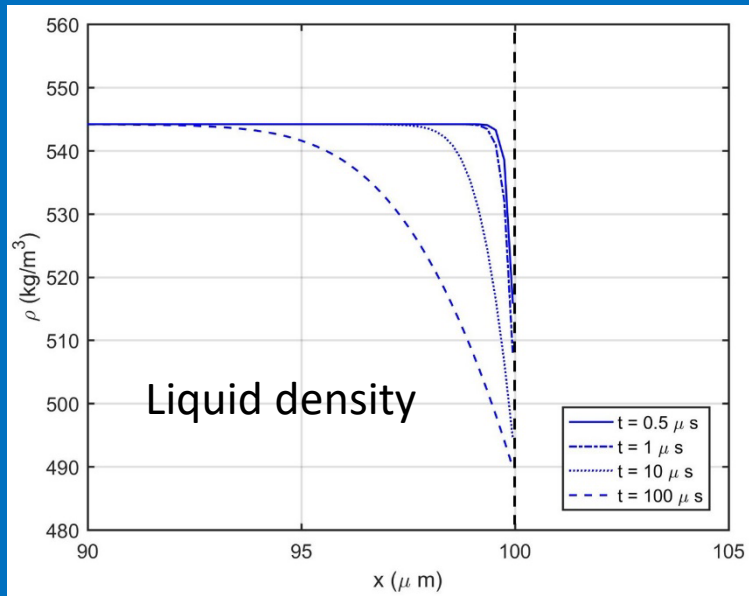
Left – temperature profile at different times at 150 bar.

- Gas-phase diffusion layer is thicker than liquid layer

- Interface temperature is approximately constant.

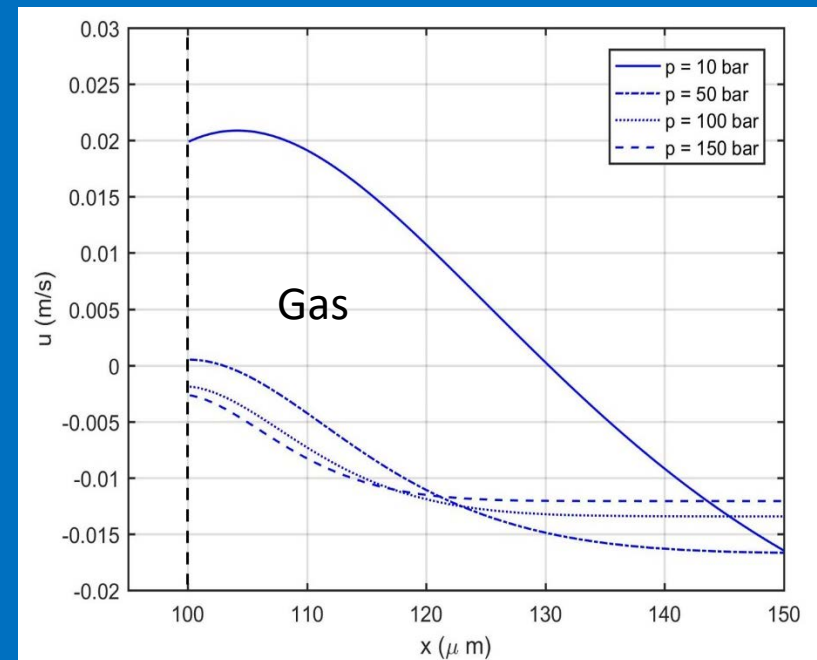
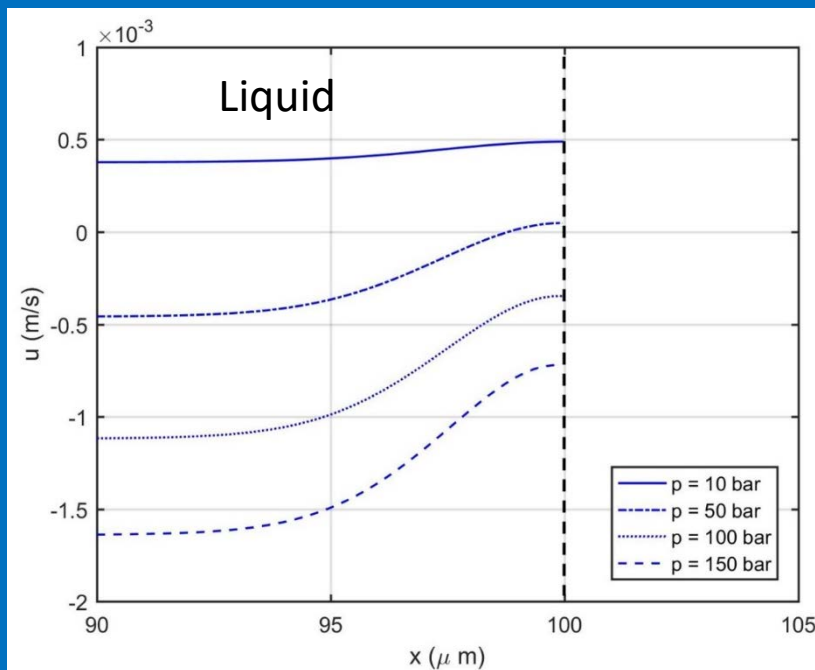
- Right – layer thicknesses grow as the square root of time.

Enthalpy and Density Development at 150 Bar: Discontinuities are found.



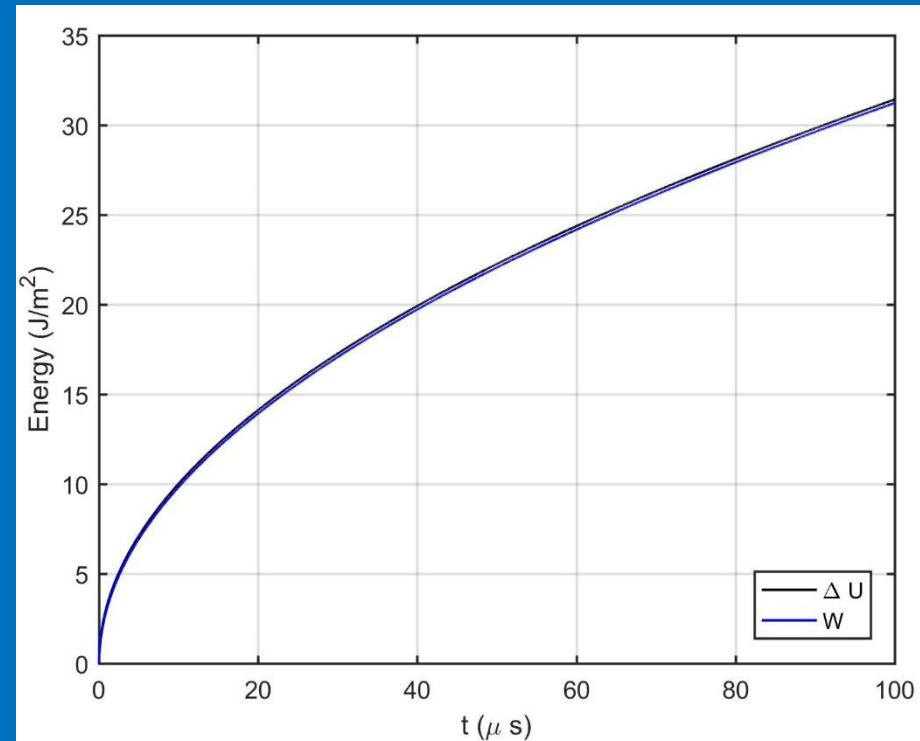
Velocity and Vaporization vs. Condensation

- Oxygen continually dissolves in the decane here.
- Decane continually vaporizes into the oxygen.
- So, which rate dominates and when?
- Positive velocity indicates net vaporization. This occurs at lower pressures.
- Negative velocity indicates net condensation. This occurs at higher pressures.



Work and Internal Energy

- The gas-liquid system is adiabatic since heat transfer is internal to the system.
- Pressure does work on a volume larger than the diffusion layers.
- At high pressure, internal energy of the liquid solution is higher than the internal energy of the gas mixture albeit at a lower temperature.
- The global (integrated) internal energy equals that work within numerical error.
- Thus, the First Law is satisfied.



Summary of Key Points

- Length scales for composition variation are vital characteristics for composition; thus, atomization is important.
- *It is widely and wrongly assumed that a liquid injected into a surrounding gas at a subcritical liquid temperature but supercritical pressure for all components, must always be treated as a continuous fluid.*
- At high pressures, gas easily dissolves in liquid and liquid easily vaporizes; surface tension and energy of vaporization are reduced but can still exist. Both phases must be considered as mixtures.
- The critical pressure of a mixture can be several times greater than the critical values for the components. Thus, critical pressure is variable over the domain as composition varies and many problems must be viewed as transcritical with both subcritical and supercritical subdomains.
- Two phases can exist well above the critical pressure of any mixture component.
- Substantial mixing occurs across phase interface; thus, fuzzy experimental images need not imply a continuous phase.

Thank You

