Interfacial and Bulk Thermodynamics in Supercritical Combustion

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Transcritical injection
Injection and heating of supercritical fluids

![Diagram showing phase changes and heating of supercritical fluids](image)

W. Mayer, H. Tamura JPP Vol. 12, 6, 1996
Injection and heating of supercritical fluids
Injection and heating of supercritical fluids

Injection and heating of supercritical fluids
Open questions

transcritical/compressible liquid

supercritical fluid

liquid vapor gas

$p_{cr}$

$T_{cr}$
Open questions

Bulk thermodynamics

Here Be Dragons

<table>
<thead>
<tr>
<th>liquid</th>
<th>vapor</th>
<th>gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_{cr} )</td>
<td>( T_{cr} )</td>
<td></td>
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</tbody>
</table>
Open questions

Bulk thermodynamics

Nitrogen into $N_2$

Mayer et al. (1998)
Open questions

Nitrogen into

Mayer et al. (1998)

Bulk thermodynamics

Here Be Dragons

$T_{cr}$

$P_{cr}$

liquid

gas

vapor

N2

N2+He
Open questions

Bulk thermodynamics

Interfacial thermodynamics

Mayer et al. (1998)

Nitrogen into

N2

N2+He

Mayer et al. (1998)
Objective and Approach

Explore the thermodynamic structure of supercritical diffusion flames to improve understanding and modeling.

Application

- Pure fluid reference data (NIST)
- Molecular dynamics (MD)
- Flame structure analysis
Methods
Large Eddy Simulation (LES)

CharLES*, developed at CTR, Stanford

- Unstructured, massively-parallelized, finite-volume, compressible code

Transcritical

- Double-flux method and entropy-stable flux implemented
- Transcritical FPV approach used for reacting cases
- Peng-Robinson EOS, Chung transport
- Ma et al. JCP 2017, AIAA 2017-0143

Khalighi et al., 2010; Bodart et al., 2013; Larsson et al., 2015
Real fluid thermodynamics for mixtures

Peng-Robinson equation of state:

\[ p = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \]

\[ a = 0.457236 \frac{(RT_{cr})^2}{p_{cr}} \left[ 1 + m(1 - \sqrt{T_r}) \right]^2 \]

\[ m = 0.3746 + 1.54226 \omega - 0.26992 \omega^2 \]

\[ b = 0.077796 \frac{RT_{cr}}{p_{cr}} \]
One fluid mixing model

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Oefelein and Yang (1998)
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One fluid mixing model - two approaches

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Oefelein and Yang (1998)

van der Waals

Mixing rules

\[ a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j \sqrt{a_i a_j (1 - k_{i,j})} \]

\[ b = \sum_{i=1}^{N} y_i b_i \]

\[ \omega = \sum_{i=1}^{N} y_i \omega_i \]

pseudocritical point

\[ T_{cr,i,j} = \left( T_{cr,i} \cdot T_{cr,j} \right)^{1/2}, \]

\[ v_{cr,i,j} = \left( \frac{1}{2} \left( v_{cr,i}^{1/3} + v_{cr,j}^{1/3} \right) \right)^3, \]

\[ Z_{cr,i,j} = \frac{1}{2} \left( Z_{cr,i} + Z_{cr,j} \right), \]

\[ p_{cr,i,j} = \frac{Z_{cr,i,j} RT_{cr,i,j}}{v_{cr,i,j}}, \]

\[ \omega_{i,j} = \frac{1}{2} \left( \omega_i + \omega_j \right). \]
1D Flame structure

- Cantera-based flamelet solver
- Peng-Robinson EOS
- Burke (2012) 8 species, 27 reactions

\[
\frac{d}{dx}(\rho u) + 2\rho V = 0, \quad V = v/r, \quad \Lambda = (\partial p/\partial r)/r
\]

\[
\rho u \frac{dV}{dx} + \rho V^2 = \frac{d}{dx}(\mu \frac{dV}{dx}) - \Lambda,
\]

\[
\rho u \frac{dY_k}{dx} + \frac{dJ_k}{dx} = \omega_k,
\]

\[
\rho u c_p \frac{dT}{dx} = \frac{d}{dx}(\lambda \frac{dT}{dx}) - \sum_k J_k \frac{dh_k}{dx} - \sum_k \omega_k h_k
\]
Molecular Dynamics (MD)

- Simulations performed in LAMMPS software using ReaxFF reactive force field.
- MD in constant NPT (# of particles, pressure and temperature) ensemble or argon.
- Pressures range from $1 - 10 \, p_{cr}$ and temperature from 110 K to 235 K at 5 K increments.
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![Graph showing RDF](image_url)

**RDF**

- Perfect crystal: 1
- Ideal gas: 1

**Reduced temperature**

- $p_t = 0.7$

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Stanford University
Bulk thermodynamics
MD fluid state-space

Argon

\[ p_r = 0.5 \]
\[ T = T_{pb} \]
\[ p_r = 9.4 \]
\[ p_r = 0.7 \]

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\[ T_r = 0.5 \]
\[ T = T_{pb} \]
\[ T_r = 1.6 \]
MD fluid state-space

Argon

\[ p_r = 9.4 \]

\[ p_r = 3.0 \]

\[ p_r = 0.7 \]

\[ Tr = 0.5 \]
\[ T = Tpb \]
\[ Tr = 1.6 \]
MD fluid state-space

Argon

- $\Tr = 0.5$
- $T = T_{pb}$
- $\Tr = 1.6$

$p = 9.4$

$p = 3.0$

$p = 1.4$

$p = 0.7$
MD fluid state-space

Argon

\[ \text{Tr} = 0.5 \quad \text{T} = \text{T}_{\text{pb}} \quad \text{Tr} = 1.6 \]

\[ \text{pr} = 9.4 \quad \text{pr} = 3.0 \quad \text{pr} = 1.4 \quad \text{pr} = 0.7 \]
MD fluid state-space

Argon

$p_r = 9.4$

$p_r = 3.0$

$p_r = 1.4$

$p_r = 0.7$

$Tr = 0.5$

$T = T_{pb}$

$Tr = 1.6$
MD fluid state-space

Argon

\[ \text{Tr} = 0.5 \quad T = T_{pb} \quad \text{Tr} = 1.6 \]

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MD fluid state-space

Argon

\[
T_r = 0.5 \quad T = T_{pb} \quad T_r = 1.6
\]

\[
pr = 9.4 \\
pr = 3.0 \\
pr = 1.4 \\
pr = 0.7
\]
What happens at the supercritical transition?

Are supercritical fluids insensitive to $dp$, $dT$?
Sub- and supercritical phase transitions

![Graph showing phase transitions with temperature and density](image)

Banuti and Hannemann PoF 2016
Sub- and supercritical phase transitions

Density $\rho$ in kg/m$^3$

Temperature $T$ in K

Isobaric specific heat capacity $c_p$ in kJ/K kg

Nitrogen

$p = 3.3$ MPa

Banuti and Hannemann PoF 2016
Sub- and supercritical phase transitions

Banuti and Hannemann PoF 2016
Sub- and supercritical phase transitions: pseudoboiling

Banuti and Hannemann PoF 2016

Stanford University
Sub- and supercritical phase transitions: pseudoboiling

Banuti and Hannemann PoF 2016
Sub- and supercritical phase transitions: pseudoboiling

Banuti and Hannemann PoF 2016
The state diagram revisited

- Nothing happens when $p_{cr}$, $T_{cr}$ is crossed.
- Instead of 4 quadrants, we see a spectrum from liquid to ideal gas at all pressures $p_r < 3$.
- The pseudoboiling-line continues the coexistence line at $p_r > 1$.
- A truly homogeneous supercritical phase does not exist until $p_r > 10$. 
Interfacial thermodynamics
Mixture fraction $Z$ - coordinate in composition space

\[ Z_H = W_H \left( 2 \frac{Y_{H_2}}{W_{H_2}} + \frac{Y_H}{W_H} + 2 \frac{Y_{H_2O}}{W_{H_2O}} + \frac{Y_{OH}}{W_{OH}} + \frac{Y_{HO_2}}{W_{HO_2}} + 2 \frac{Y_{H_2O_2}}{W_{H_2O_2}} \right) \]

Lacaze & Oefelein CnF 2012
Envelope of physical flamelets
Envelop of physical flamelets

This is the variation we can expect at

\( T_{\text{LOX}} = 120 \text{ K}, \ T_{\text{GH2}} = 295 \text{ K}, \ p = 7 \text{ MPa} \)
Pseudocritical point

\[ p_{cr,1}, p_{cr,2} \]

\[ T_{cr,1}, T_{cr,2} \]

Fluid A

Fluid B

pseudo-pure fluid
Pseudocritical point

$T_{cr,1}$ $T_{cr,2}$

$p_{cr,1}$ $p_{cr,2}$

mixture

Fluid A

Fluid B

pseudo-pure fluid
Pseudocritical point

Reid et al. 1987

\[ T_{\text{mix,cr}} = \sum_{\alpha=1}^{N_S} X_\alpha T_{\alpha,\text{cr}}, \]

\[ p_{\text{mix,cr}} = \frac{RT_{\text{mix,cr}} \sum_{\alpha=1}^{N_S} X_\alpha Z_{\alpha,\text{cr}}}{\sum_{\alpha=1}^{N_S} X_\alpha v_{\alpha,\text{cr}}}. \]
Pseudocritical point

Reid et al. 1987

\[ T_{\text{mix},\text{cr}} = \sum_{\alpha=1}^{N_S} X_\alpha T_{\alpha,\text{cr}}, \]

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Local mixture thermodynamic state

Lacaze and Oefelein  CnF 2012
Local mixture thermodynamic state

\[ T_{\text{mix,cr}} = \sum_{\alpha=1}^{N_S} X_\alpha T_{\alpha,cr}, \]

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Local mixture thermodynamic state

\[ T_{\text{mix,cr}} = \sum_{\alpha=1}^{N_S} X_{\alpha} T_{\alpha,cr}, \]

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Local mixture thermodynamic state

Lacaze and Oefelein  CnF 2012

\[ T_{\text{mix,cr}} = \sum_{\alpha=1}^{N_S} X_\alpha T_{\alpha,\text{cr}}, \]

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\[ T_r = \frac{T}{T_{\text{cr}}} \]

\[ p_r = \frac{p}{p_{\text{cr}}} \]
Local mixture thermodynamic state

\[ T_{\text{mix, cr}} = \sum_{\alpha=1}^{N_S} X_\alpha T_{\alpha, cr}, \]
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\[ T_r = \frac{T}{T_{cr}}, \quad p_r = \frac{p}{p_{cr}} \]

Lacaze and Oefelein  CnF 2012
'Ribbon' chart maps all flame trajectories into $p_r / T_r$.

\[ T_{LOX} = 120 \text{ K} \]
\[ T_{GH2} = 295 \text{ K} \]
\[ p = 7 \text{ MPa} \]

\[ p_r = \frac{p}{p_{cr}} \quad T_r = \frac{T}{T_{cr}} \]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>H$_2$</th>
<th>O$_2$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{cr}$ [K]</td>
<td>33.0</td>
<td>154.58</td>
<td>647.10</td>
</tr>
<tr>
<td>$p_{cr}$ [MPa]</td>
<td>1.284</td>
<td>5.043</td>
<td>22.064</td>
</tr>
<tr>
<td>$v_{cr}$ [cm$^3$/mol]</td>
<td>64.28</td>
<td>73.37</td>
<td>55.95</td>
</tr>
<tr>
<td>$\omega$</td>
<td>-0.216</td>
<td>0.022</td>
<td>0.344</td>
</tr>
</tbody>
</table>
Variation of conditions – intuitive assessment
Mixing and transition to ideal gas

At transition to ideal gas, \( Y_{O_2} > 98\% \)

\[
Z = \frac{p}{\rho RT} = \frac{p_{\text{real}}}{p_{\text{ideal}}}
\]

\( T_{LOX} = 120 \text{ K, } T_{GH2} = 295 \text{ K, } p = 7 \text{ MPa} \)
Mixing and transition to ideal gas in LES

Ruiz et al. AIAAJ, 2016
Transcritical shear layer
Where do we need a real gas EOS?

\[
Z = \frac{p}{\rho RT} = \frac{p_{\text{real}}}{p_{\text{ideal}}}
\]

Z ideal > 0.95
Where do we need real gas mixing rules?

Real fluid

Real mixing

\[ Z < 0.95 \]

\[ Y_{O2} < 0.99 \]
Mixing and transition to ideal gas in LES

\[ Z = \frac{p}{\rho RT} = \frac{p_{\text{real}}}{p_{\text{ideal}}} \]

Also:
Banuti et al. CnF 016, based on Oefelein & Yang 1998
Lacaze & Oefelein 2012
Conclusions

Bulk
• Bulk pure fluid thermodynamics are relevant!
• Two thermodynamic transitions - Pseudoboiling - Ideal gas

Interface
• Mixing occurs essentially in ideal gas
• Only very thin real mixing layer
• Real fluid behavior is essentially confined to pure oxygen
\[ Z = \frac{p}{\rho RT} = \frac{p_{\text{real}}}{p_{\text{ideal}}} \]
LOX/GH2 Vapor liquid equilibrium

Yang (2000)
Transcritical shear layer

\[ Z = \frac{p}{\rho RT} = \frac{p_{\text{real}}}{p_{\text{ideal}}} \]

Z = 0.95