Supercritical pseudoboiling for general fluids and its application to injection

By D.T. Banuti, M. Raju and M. Ihme

1. Motivation and objectives

Transcritical injection has become an ubiquitous phenomenon in energy conversion for space, energy, and transport. Initially investigated mainly in liquid propellant rocket engines (Candel et al. 2006; Oefelein 2006), it has become clear that Diesel engines (Oefelein et al. 2012) and gas turbines operate at similar thermodynamic conditions. A solid physical understanding of high-pressure injection phenomena is necessary to further improve these technical systems. This understanding, however, is still limited. Two recent thermodynamic approaches are being applied to explain experimental observations: The first is concerned with the interface between a jet and its surroundings, in the pursuit of predicting the formation of droplets in binary mixtures. Dahms et al. (2013) have introduced the notion of an interfacial Knudsen number to assess interface thickness and thus the emergence of surface tension. Qiu & Reitz (2015) used stability theory in the framework of liquid - vapor phase equilibrium to address the same question. The second approach is concerned with the bulk behavior of supercritical fluids, especially the phase transition-like pseudoboiling (PB) phenomenon. PB-theory has been successfully applied to explain transcritical jet evolution (Oschwald & Schik 1999; Banuti & Hannemann 2016) in nitrogen injection. The objective of this paper is to generalize the current PB-analysis. First, a classification of different injection types is discussed to provide specific definitions of supercritical injection. Second, PB theory is extended to other fluids – including hydrocarbons – extending the range of its applicability.

2. Supercritical phase transitions

Before an injection process can be analyzed, we need to discuss the thermodynamic phase plane of fluids and its relevance to injection.

2.1. Pseudoboiling and Nishikawa-Widom line

Vaporization is an equilibrium phase transition from liquid to vapor at the saturation temperature with discontinuous changes in density and enthalpy. Such a process is depicted in Figure 1 for oxygen at a pressure of 4 MPa. The subcritical transition exhibits a diverging specific isobaric heat capacity, as the temperature stays constant while energy is added. At the supercritical pressure of 10 MPa, Figure 1 shows that the discontinuous change in density has vanished. However, there still exists a distinct temperature at which heat capacity and thermal expansion exhibit pronounced extrema, causing a phase change-like behavior of the fluid when heating through this temperature range. This transition state is referred to as the supercritical pseudoboiling phenomenon (Oschwald et al. 2006; Banuti 2015).

The supercritical heat capacity peaks line up and form an extension to the coexistence line; Figure 2 shows this line in a $p$-T diagram. Nishikawa & Tanaka (1995) were the
Figure 1. Density (dashed lines) and specific isobaric heat capacity (solid lines) for a sub- and a supercritical pressure. The supercritical transition through pseudoboiling, indicated by the finite peak in $c_p$, is similar to subcritical vaporization when maxima in thermal expansion and heat capacity are regarded. Data for oxygen from NIST, (Linstrom & Mallard 2016).

Figure 2. Fluid phase diagram in terms of the reduced temperature $T_r = T/T_{cr}$ and reduced pressure $p_r = p/p_{cr}$. The reduced heat capacity is nondimensionalized with the ideal gas value $c_{p,r} = c_p / ((γR)/(γ − 1))$. The Nishikawa-Widom line forms an extension to the coexistence line and divides liquid and gaseous states. An ideal gas state is reached at higher temperatures, as $Z \to 1$.

first to measure the dramatic changes in fluid properties upon crossing this curve, which divides liquid-like and gas-like fluid states, even at supercritical pressures.

The compressibility factor $Z$ measures the deviation of fluid behavior from ideal gas behavior. It is defined as $Z = p/\rho RT$. Figure 2 shows that a fluid at supercritical pressure needs to be heated to approximately twice the critical temperature before it can be considered an ideal gas. Thus, there is no contradiction between a fluid being in a supercritical state and in behaving like an ideal gas.
Under many conditions, however, this mechanism must be ruled out. Generally not the case, and modern theory still lacks a first principle. [8,9]. Sirignano et al. [12,13], Delplanque [14], and Sirignano [15] investigated the mixing process and fluid disintegration in cluster drop simulations considering Soret and Dufour effects to perform using proposed new subgrid-scale terms, denoted "terms, in concert with typical subgrid-scale flux terms."

Table 1. number - both of which are functions of surface tension. The characterization is carried out in terms of the Ohnesorge or the Weber number. The presented analysis also quantifies and explains the behavior of the inherent dense multicomponent mixtures.

3. Towards a classification of supercritical injection

Jet break-up regimes are typically presented in the Reitz diagram for single jets, or in the Chigier diagram for coaxial jets (Kuo & Acharya 2012). In addition to the Reynolds number, the characterization is carried out in terms of the Ohnesorge or the Weber number - both of which are functions of surface tension. 

Figure 4 shows two results of a classical injection experiment by Mayer et al. (1998). Injection at subcritical pressure exhibits a distinct interface as a sign of a finite surface tension. The aforementioned classification is thus possible. In contrast, injection at supercritical pressure resembles turbulent mixing of gaseous jets; the effect of surface tension is negligible. Thus, the current classification is not suitable to analyze supercritical injection.

How can we distinguish different supercritical disintegration modes? Figure 5 defines processes A to E and compiles the respective shadowgraphs; conditions are shown in Table 1.
Figure 5. Left: Injection processes in $p - T$ diagram, with coexistence line (solid) and Nishikawa-Widom line (dashed). Right: Visualizations of corresponding injection regimes. Conditions in Table 1. A and B are modified from Chehroudi et al. (2002), C is modified from Lamanna et al. (2012), D from Branam & Mayer (2003), and E is modified from Stotz et al. (2011).

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_{r,in}$</th>
<th>$p_{r,in}$</th>
<th>$T_{r,\infty}$</th>
<th>$p_{r,\infty}$</th>
<th>Jet</th>
<th>Chamber</th>
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<tbody>
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<td>A</td>
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<td>≈0.23</td>
<td>2.38</td>
<td>0.23</td>
<td>$N_2$</td>
<td>$N_2$</td>
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<tr>
<td>B</td>
<td>0.71-0.87</td>
<td>≈1.23</td>
<td>2.38</td>
<td>1.23</td>
<td>$N_2$</td>
<td>$N_2$</td>
</tr>
<tr>
<td>C</td>
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<td>1.9</td>
<td>0.02</td>
<td>$C_6H_{14}$</td>
<td>Ar</td>
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<tr>
<td>D</td>
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<td>≈1.77</td>
<td>2.36</td>
<td>1.77</td>
<td>$N_2$</td>
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<td>E</td>
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<td>6.59</td>
<td>1.9</td>
<td>0.16</td>
<td>$C_6H_{14}$</td>
<td>Ar</td>
</tr>
</tbody>
</table>

Table 1. Conditions of visualizations in Figure 5. Reduced values with respect to injected fluid.

Process A is the subcritical jet treated in Reitz’ diagram. Increasing surrounding and injection pressure above the supercritical value leads to case B. In C, a supercritical fluid close to the critical point is injected with a large pressure drop. D is reached when the injection temperature of B is raised. Finally, increasing the temperatures of C leads to process E.

From the five cases visualized in Figure 5, three groups can be distinguished: Case A is the classical liquid jet with a distinct surface. Cases B and D are similar but, due to negligible surface tension effects, exhibit a more convoluted and diffuse interface. Cases C and E are remarkably different from the previous cases, showing a high-pressure jet expanding in a lower-pressure environment, similar to ideal gas expansion into vacuum.

Types B and D deserve more discussion as they are representative for Diesel and rocket engines. As the injection temperature increases, the injection density decreases, resulting in the reduced density ratio of case D. Note that the injection density is very sensitive to the injection temperature around the pseudoboiling temperature (see Figure 1), with associated challenges for experiments and their evaluation. If the temperature of case D is increased to more than twice the critical temperature, D will have gradually changed to an ideal gas jet (see Figure 2).

Classically, any isobaric injection process crossing the critical temperature is referred to as transcritical injection. We see that case D strongly resembles case B. Both have in common that they cross the Nishikawa-Widom line. We will use supercritical injection as a generic term encompassing any of the cases B to E.
3.1. A thermodynamic definition of the supercritical boundary

Figure 5 indicates that case B does not have a sharp interface, unlike case A. Nonetheless, the outline of the jet is clearly discernible in the shadowgraph. The question is, how do we define the boundary of such a supercritical jet?

One approach is to use the arithmetic mean of the injected and surrounding density (Jarczyk 2013). This definition of the boundary depends on the process parameters: when we change the injection or surrounding temperature (and thus density), our definition of the boundary in terms of density will also change. In contrast, the boundary of the subcritical case A is uniquely identified regardless of injection temperature, because it is associated with a thermodynamic state instead of a process parameter. Figure 1 illustrates that the interface will always be present at saturation conditions, even if inflow conditions or surrounding conditions are varied.

An analogous definition for transcritical injection is to use the pseudoboiling state as a unique marker. It, too, is associated with large gradients in density \((\partial \rho / \partial T)_{p}\), and is a purely thermodynamic condition. Figure 6 compares the jet core determined from the arithmetic density mean (top) to the thermodynamic pseudoboiling condition (bottom). Both yield comparable results for the presented case, but the thermodynamic definition resolves any ambiguity.

3.2. The latent heat of supercritical fluids

The latent heat diminishes for increasing pressure as the fluid approaches the critical point. However, counterintuitively, the supercritical heating process B in Figure 5 does not require less energy than the subcritical process A.

Energy needs to be supplied to the liquid when heating to an ideal gas state to overcome
intermolecular forces, regardless of whether the pressure is sub- or supercritical. High pressure real fluid effects merely distribute this latent heat over a finite temperature interval. We can interpret the required energy input during pseudoboiling – signified by the excess heat capacity that needs to be overcome – as a nonequilibrium latent heat of vaporization.

Figure 7 illustrates this quantitatively by plotting enthalpy versus temperature for three pressures. The fluid is oxygen, a pressure of 4 MPa constitutes a subcritical condition, and 6 MPa and 10 MPa are supercritical. Towards lower temperatures, all isobars converge towards the same liquid enthalpy asymptote $h_L(T)$; towards higher temperatures, the isobars converge towards the same ideal gas enthalpy asymptote $h_{iG}(T)$. Note that both asymptotes are pressure independent. Thus, the transition from a liquid to an ideal gas state is energetically identical, regardless of pressure. This is exemplified in Figure 7 for the transition from $T_L = 130$ K to $T_G = 460$ K, which requires the same $\Delta h_{LG}$ at all shown pressures.

Intermolecular forces do not just vanish when a liquid is compressed beyond the critical pressure; the energy needed to overcome these forces needs to be supplied regardless of pressure.

4. A pseudoboiling-line for general fluids

We have discussed the fact that the pseudoboiling process is not merely an abstract thermodynamic concept, but has very specific implications about understanding and interpreting high-pressure injection. It is thus desirable to predict where this phase change occurs, i.e., we seek an equation for the location of the Nishikawa-Widom line.

4.1. Nishikawa-Widom line for simple fluids

A suitable relation between the reduced pressure $p_r$ and reduced temperature $T_r$ is

$$p_r = \exp \left[ A (T_r - 1) \right]; \quad A = 5.5,$$

(4.1)
for the simple fluids O\textsubscript{2}, N\textsubscript{2}, and Ar (Banuti (2015)). Figure 8 shows good agreement between Eq. (4.1), and data of heat capacity peaks for nitrogen, oxygen, and argon. However, Figure 8 also shows that the relation fails for water and hydrogen. This is a serious shortcoming, as hydrogen and water play an important role in combustion. Similarly, Eq. (4.1) fails for hydrocarbons.

4.2. Nishikawa-Widom line for general fluids

Figure 8 not only demonstrates the shortcoming of Eq. (4.1), but also suggests a remedy: instead of a constant $A$, a fluid-dependent coefficient $A_s$ is introduced and determined for each species,

$$p_r = \exp \left[ A_s \left( T_r - 1 \right) \right]; \quad A_s \text{ species dependent.} \quad (4.2)$$

Table 2 provides $A_s$ for a wide range of fluids, including hydrocarbons up to n-hexane. Comparison with the acentric factor $\omega$, also provided in Table 2, suggests an essentially linear relation, which is confirmed in Figure 9. Thus, Eq. (4.2) can be recast in terms of $\omega$ as

$$p_r = \exp \left[ A_\omega \left( T_r - 1 \right) \right]; \quad A_\omega = 5.29 + 4.35\omega, \quad (4.3)$$

allowing for a fast evaluation without requiring fluid $p-v-T$ data.

4.3. An improved fitted relation

Equation (4.3) is convenient in its ease of parameter determination from the tabulated acentric factor; Figure 8 hints at another shortcoming of Eq. 4.1: while the Nishikawa-Widom line is a straight line in a log-linear $p-T$ plot, water and hydrogen exhibit a significant curvature of their graphs.

To incorporate this deviation, a modified expression is proposed in the form

$$p_r = \exp \left[ A' \left( T_r - 1 \right)^a \right]; \quad A', a \text{ species dependent.} \quad (4.4)$$

Data for $A'$ and $a$ are obtained by fitting and are compiled in Table 2.

Figure 10 compares Eq. (4.1) using $A$, Eq. (4.2) using $A_s$, and Eq. (4.4) using $A'$ and
Table 2. Acentric factor $\omega$ and slope of the Nishikawa-Widom-line for a number of species obtained from NIST Linstrom & Mallard (2016). $A_s$ for Eq. (4.2), $A', a$ for Eq. (4.4). Results are clustered (from top to bottom) as quantum gases, noble gases, diatomic molecules, hydrocarbons, and other complex molecules.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\omega$</th>
<th>$A_s$</th>
<th>$A'$</th>
<th>$a$</th>
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<td></td>
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<td>He</td>
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Figure 9. Linear relation between fluid acentric factor $\omega$ and the parameter $A$ of the Nishikawa-Widom-line Eq. (4.2).
Figure 10. Comparison of Nishikawa-Widom-line fluid data (symbols) and correlations Eq. (4.1) with $A$, Eq. (4.2) with $A_s$, Eq. (4.4) with $A', a$.

It can be seen that Eq. (4.4) offers the best accuracy over a wide range of acentric factors and can accurately capture the curvature of non-simple fluids.

5. Conclusions

The present paper discusses some implications of supercritical thermodynamics for injection problems, relevant to rocket engines, gas turbines, and Diesel engines.

Break-up processes are typically classified in terms of the ratio between surface tension forces to inertial or viscous forces. This classification is not always applicable to supercritical injection, as the surface tension may vanish. We demonstrate that injection pressure ratio and temperature interval are a useful approach to analyze supercritical injection.

The most prominent feature of the supercritical state space is the Nishikawa-Widom line, which is defined as the locus of specific isobaric heat capacity peaks. Pseudoboiling is the supercritical nonequilibrium phase change that occurs when the Nishikawa-Widom line is crossed. We demonstrate that the energy required to heat a fluid from a subcritical liquid temperature to an ideal gas state is identical at sub- and supercritical pressures, despite the vanishing latent heat with increasing pressure. This can be interpreted as a distributed latent heat.

We find that the Nishikawa-Widom line is well described by $p_r = \exp[A_\omega(T_r - 1)]$, with $A_\omega = 5.29 + 4.35\omega$. The acentric factor $\omega$ can be found in fluid data tables. This relation offers a reliable and convenient way to predict the temperature at which many thermodynamic and transport properties exhibit the strongest gradients or extrema for a wide range of fluids.

The pseudoboiling condition can also be used to define a thermodynamically unique and consistent boundary of a transcritical jet, analogous to the subcritical liquid–gas interface.
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