Simulating Retrograde Condensation in a Shock Tube

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Abstract

Retrograde condensation of pure species is investigated using a one-fluid model and a homogeneous phase equilibrium model based on entropy maximization. Fluid dynamics simulations are performed to model the retrograde condensation process of a fluorinated compound in a shock tube. To our knowledge, the present simulations are the first CFD simulation of retrograde condensation processes. The computations show reasonably good agreement with available experimental data, both quantitatively and qualitatively. Both simulations and experiments show that condensation occurs after the high pressure reflected shock is formed from the end wall. Increase in the initial pressure ratio increases the incident shock strength and reinforces condensation by elevating the liquid volume fraction. A complete liquefaction shock is found at high incident shock Mach numbers when the compression is strong enough to send the fluid from the pure vapor to the pure liquid state by crossing the two-phase mixture region. After condensation, the condensed liquid phase is fully depleted as the pressure wave expands and the fluid is brought back to the vapor state though a continuous evaporation process.

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Introduction
Phases transition is a central topic in common applica
tions, such as in diesel engines and gasoline-direct-injection (GDI) engines. Because the energies are
stored in the liquid fuels, preparation of gaseous fuel through the injection, spray, and atomization is an
important physical process that needs detailed understanding. This is especially true for the mixing-controlled
type combustion, such as conventional diesel spray combustion, for which mixture formation is more cr
for the combustion processes.

Condensation is a common phase transition phe
nomenon. Usually, it occurs for species experiencing an expansion process. Species exhibiting such characte
istics are referred to as regular or simple species. This
kind of condensation has been experimentally observed
in supersonic nozzles for water [1-3]. However, condensa
tion due to compression was not studied until the ear
ly work of Thompson, who investigated compression
condensation both analytically, using thermody
namic analysis [4], and experimentally in a shock tube
occurs for species that have a large number of molec
ular degrees of freedom (i.e., large heat capacity), and as
a result, compression work can be stored as internal energy with only a small temperature rise [4].

Condensation Mechanisms
The distinctive and different behavior of regular
and retrograde fluids is illustrated in Figure 1, which
presents the temperature-entropy phase diagram of pure
ethylenes (C\textsubscript{2}H\textsubscript{4}), a regular species, and perfluorohepta
tane (C\textsubscript{7}F\textsubscript{16}), a retrograde species that is used in the
simulations to be presented later. The thermodynamic
properties used for the two species are obtained from
DIPPR database [6]. In Fig. 1, the up arrow represents
an isentropic compression process (through which tem
perature and pressure increase) while the down arrow
stands for an isentropic expansion process (through
which temperature and pressure decrease). More specifi
cally, for C\textsubscript{2}H\textsubscript{4}, whether it is initially in the pure liquid
or vapor phase, only through an expansion process will
the fluid enter the two-phase region with condensation.
In this paper, the two-phase region stands for vapor-
liquid equilibrium and the solid state is not considered.
For C\textsubscript{7}F\textsubscript{16}, however, there are two separate scenarios. If
the fluid is initially in the vapor phase, only compres
sion can bring the fluid into the two-phase region with
condensation. In contrast, if the fluid is initially in the
liquid phase, only an expansion can bring the fluid into
the two-phase region with evaporation.

Equation of State
To consider the non-ideality of thermodynamic
properties at high pressures, a proper equation of state
(EOS) is needed. The Peng-Robinson EOS [7] is used
because it has also been successfully applied to study
droplet evaporation at high-pressure conditions [8, 9]. It
is also the most popular equation of state used in the
gas and oil industry. The Peng-Robinson EOS reads:

\[ P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{1} \]

where \( P \) is pressure, \( T \) is temperature, \( v \) is the molar
volume. \( a \) and \( b \) are two parameters determined from:

\[
\begin{align*}
\alpha &= 1 + \kappa \left( 1 - \sqrt{\frac{T_c}{T}} \right)^2 \\
\kappa &= 0.37464 + 1.54226 \omega - 0.26992 \omega^2
\end{align*}
\tag{3}
\]

with \( T_c, P_c, \) and \( \omega \) are the critical temperature, pressure
andacentric factor, respectively. In case of a mixture,
the classical Van der Waals mixing rule is used:

\[
\begin{align*}
\alpha &= \sum_{i} \sum_{j} x_i x_j a_{ij} \\
b &= \sum_{i} x_i b_i \\
a_{ij} &= \left( 1 - \delta_{ij} \right) \sqrt{a_i a_j}
\end{align*}
\tag{4}
\]

where, \( x_i \) is the mole fraction of species \( i \) in the mixt
ure. \( \delta_{ij} \) is the interaction parameter between comp
onents \( i \) and \( j \).

This EOS model has been used to calculate the sat
uration pressure line of a pure species by enforcing the
equality of fugacity for vapor-liquid equilibrium. Figure
2 shows the calculated vapor-liquid saturation line for
pure perfluoroheptane. The overall match is very good
for the entire range of conditions of vapor-liquid equ
librium.

Phase Equilibrium Model
A homogeneous phase equilibrium model is adopt
ed. This model assumes that (1) the two phases have the
same velocity, temperature and pressure; (2) thermody
namic equilibrium is attained instantaneously. To de
termine the global thermodynamically stable state in
each computation cell, based on the entropy maximiza
tion principle, the following set of equations must be
solved [10-11]

\[
\begin{align*}
\lambda \rho_V u_V + (1 - \lambda) \rho_L u_L &= \rho^{spec} u^{spec} \\
\lambda &= (\rho^{spec} - \rho_L) / (\rho_V - \rho_L) \\
P &= P^\circ(T) \\
f_V &= f_L
\end{align*}
\tag{6}
\]
Superscript “spec” stands for specified inputs to the thermodynamic solver. Subscripts “V” and “L” refer to the vapor and liquid phase, respectively. $\lambda$ is the volume fraction of the vapor phase; $P^s$ is the saturation pressure of the pure species; $f$ is the fugacity. $\rho$ is the mass density.

**Results and Discussion**

In the experiments [5], the shock tube was composed of a driver section of 250 cm and a driven section of 242.6 cm. The driver section was filled with nitrogen and the driven section used a fluorinated compound, perfluoro-dimethyccyclohexane (C₈F₁₆). Since available thermodynamic properties of this species are limited, a similar species with available property data, perfluoro-heptane (C₇F₁₆) was used instead in the present simulations.

A 1-D domain was selected using 1500 grid points for each section. Together three different initial conditions are considered for the driven section: 0.51, 0.67 and 0.99 bar. The open-source computational fluid dynamics (CFD) code KIVA-3V Release 2 [12] was used as the basic fluid solver. The standard KIVA code uses ideal gas relations. To consider real gas effects with the Peng-Robinson equation of state model, the thermodynamic relationships were modified. Some details can be found in Refs. [7, 13-14].

The shock tube experiment [5] was designed to produce liquefaction as the incident shock reflects from the closed end of the tube. The driver section is at State 4 while the driven section is at State 1. Upon releasing the diaphragm, incident compression shock and expansion waves form. The state behind the incident shock front is State 2. The section between contact surface and the leading expansion wave is at State 3. Finally, the region between the reflected shock wave and the contact surface is at State 5.

The effects of the incident shock Mach number ($M_s$) are shown in Fig. 3. Figure 3 (a) shows that pressure $P_2$ downstream of the incident shock does not show a strong non-linear behavior, as would be predicted for ideal gases from the normal shock relations. In contrast, real gas effects lead to an almost-linear relationship. The pressure $P_3$ and temperature $T_3$ are shown in Figs. 3 (b) and (c). As the shock strength increases, $P_3$ increases too. It is noted that the profile of $P_3$ does not show liquefaction effects, as there are no obvious changes in its slope, as also noticed in Ref. [5]. On the contrary, the plot of $T_3$ is a good indication of the onset of condensation, which shows a “distorted, angular S-form” [5]. The two discontinuities on the slope of $T_3$ represent the start of partial and complete condensation, respectively [5]. The shock Mach number required for partial and complete condensation is specifically marked in the plots of Fig. 3. Figure 3 (d) plots $P_5$ versus $T_5$ with the saturation line. It is clearly seen that the fluid in State 5 experiences a state change from superheated vapor to a two-phase mixture, and then to a compressed liquid and finally to the supercritical state.

Two special cases were chosen for further analyses. Case 1 has partial condensation occurring at $P_1=0.67$ bar and $P_2=4.0$ bar. Case 2 is at $P_1=0.99$ bar and $P_2=8.5$ bar, under which strong (actually complete) condensation occurs. To aid in visualizing the location and onset of condensation, corresponding x-t wave diagrams were generated, as seen in Fig. 4. The colors are based on the pressure values, but to increase the color contrast, the logarithm of pressure is used). Figures 4 (c) and (d) are blow-up plots for these two cases, focusing on the right-hand end region to illustrate the complex wave characteristics.

For Case 1, the predicted contours, including temperature, pressure, liquid volume fraction and compressibility factors, are plotted in Fig. 5 at $t=16.0$ ms ((a) and (c)) and $t=18.0$ ms ((b) and (d)). These two time instants are after the reflected shock has formed. The liquid volume fraction has already reached 2% by $t=16.0$ ms. It is noticed that there is a plateau of temperature and pressure in the condensation region, which corresponds to the relationship between temperature and saturation pressure. Because of the phase change, a large pressure gradient appears. From $t=16.0$ to $t=18.0$ ms, the two-phase region is transported along with the pressure wave, and the previous temperature and pressure gradients are disrupted. Compared with the results at $t=16.0$ ms, the decrease of liquid volume fraction indicates that evaporation continues to occur while the local fluid is experiencing expansion.

Results for Case 2 are presented in Figure 6 at two instants. Condensation has already occurred at $t=13.28$ ms. But, at this time the condensation is so strong that a full condensation, i.e., a complete liquefaction shock, occurs. The shock strength is so high that 100% of the original pure gaseous fluid is converted to the liquid phase by the heat removal at the right-hand end of the tube. Therefore, a larger local gradient is found for both the pressure and temperature when compared with Case 1. The effects are more obvious from the compressibility factor contours for the vapor phase, which experiences an abrupt increase in the two-phase region. At $t=15.0$ ms, the liquid phase amount has dropped as evaporation occurs, similar to Case 1. However, since the vapor-liquid interface is distinctive due to the strong liquid volume fraction gradient, the evaporative cooling leads to a sharp change of pressure, temperature and the compressibility factor.

The two numerical simulations above indicate that partial or complete condensation does occur when the reflected shock forms as the incident shock is reflected from the closed end of the tube. Because pressure is enhanced through the reflected shock (e.g., also seen through the color scale), the appearance of the liquid
phase can only be due to the compression, but not through successive expansion (such as the condensation seen in nozzles, as mentioned above). Therefore, the present CFD simulation results are consistent with the condensation mechanism for this retrograde fluid based on previous thermodynamic analysis (refer to Fig. 1 (b)). In addition, it is remarked that the possible condensation region is limited to lie between the contact surface and the right-hand end of the tube, where the pressure is high enough to be able to trigger the phase change.

Conclusions

Computational fluid dynamic simulations were performed for two-phase flows in a shock tube to investigate the retrograde condensation behavior of a pure species. To consider real gas effects, the Peng-Robinson equation of state was used. A homogeneous phase equilibrium model based on entropy maximization was used as the phase transition model based on the open source KIVA code.

The simulation results conform to the expected behavior from thermodynamic analyses based on temperature-entropy phase diagrams, and the deduced condensation mechanisms for the different fluids. For the retrograde fluid, the present shock tube simulations with a fluorocarbon fluid were found to predict well both qualitatively and quantitatively when compared with available experimental data. Specifically, the following conclusions can be drawn from the present simulations and the comparisons with the classical experiments of Dettleff [5]:

1. Consistent with the experiments, condensation occurs in the reflected shock region at the right-hand end of the shock tube, where only the retrograde fluid exists.
2. Partial condensation occurs when the incident shock is strong enough that the fluid can be compressed from the vapor state to the two-phase mixture state.
3. Complete condensation occurs when the incident shock is strong enough that the fluid can be further compressed from the vapor state to the two-phase mixture state, and to the compressed liquid state or supercritical state with liquid-like properties.
4. The temperature at State 5 (behind the reflected shock) is a better indicator of condensation than pressure.
5. Later after the condensation, the expanding wave leads to continuous evaporation until the liquid phase is fully depleted.

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References

Figure 1. Temperature-entropy phase diagram of pure species. (a): Regular fluid Ethylene (C$_2$H$_4$). (b) Retrograde fluid perfluoroheptane (C$_7$F$_{16}$). Upper arrow stands for an isentropic expansion process while the lower arrow an isentropic compression process.

Figure 2. Comparison of predicted saturation pressure using Peng-Robinson equation of state with DIPPR data for pure perfluoroheptane (C$_7$F$_{16}$). Note pressure is shown in a logarithmic scale.
Figure 3. (a) Comparison with experimental data as a function of incident shock Mach number. (a): Pressure $P_2$, (b): Pressure $P_5$, (c): Temperature $T_5$. The two discontinuities of slope represent onset of partial condensation and complete condensation, respectively. (d): Pressure $P_5$ versus temperature $T_5$. 
Figure 4. Calculated x-t wave diagram for the partial and complete liquefaction shocks. (a) and (c): $P_1=0.67$ bar and $P_4=4.0$ bar. (b) and (d): $P_1=0.99$ bar and $P_4=9.5$ bar. The contact surface is represented in blue lines in (a) and (b), but black lines in the blow-up plots (c) and (d) to increase the color contrast.
Figure 5. Predicted contact discontinuity, liquid volume fraction, compressibility factor of two phases, temperature and pressure for partial liquefaction shock at $P_1=0.67$ bar and $P_4=4.0$ bar. (a) and (c): At 16.0 ms. (b) and (d): At 18.0 ms. Note that the liquid volume fraction is enlarged by 10 times. Dashed line colored with magenta indicates the right-hand end wall location.
Figure 6. Predicted contact discontinuity, liquid volume fraction, compressibility factor of two phases, temperature and pressure for complete liquefaction shock at \( P_1 = 0.99 \) bar and \( P_4 = 9.5 \) bar. (a) and (c): At 13.28 ms. (b) and (d): At 15.0 ms. Dashed line colored with magenta indicates the right-hand end wall location.